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Technical Note

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By T. Torres

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**TREATMENT TECHNOLOGIES  
FOR HAZARDOUS ASHES  
GENERATED FROM POSSIBLE  
INCINERATION OF  
NAVY WASTE**

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**ABSTRACT** The Navy recognizes that thermal treatment of Navy hazardous wastes (HW) should, under the terms of the Resource Conservation and Recovery Act of 1976, be avoided. Combustion waste disposal may nonetheless become unavoidable in certain cases, even after all possible process enhancements that avoid HW production are implemented. Even then, some toxic constituents that may be present in the waste will not be destroyed by incineration and will persist in the ash residue produced by incineration. Such incinerator ashes will have to be disposed of in HW landfills. The Navy is thus evaluating methods of treatment of such ash to remove or immobilize the toxic constituents that persist following incineration in order to render the waste treatment residue nonhazardous. Appropriate technology identified in this work can be applied to ash produced by HW combustors operated by the Navy, if any, or be required for ash produced by commercial generators handling Navy HWs.

NAVAL CIVIL ENGINEERING LABORATORY PORT HUENEME CALIFORNIA 93043-5003

# METRIC CONVERSION FACTORS

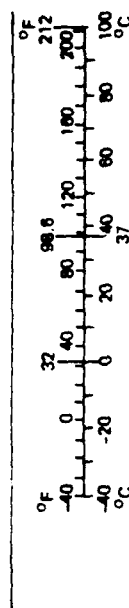
## Approximate Conversions to Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
in ft yd mi	inches	2.54	centimeters	cm
	feet	30	centimeters	cm
	yards	0.9	meters	m
	miles	1.6	kilometers	km
<b>AREA</b>				
in <sup>2</sup> ft <sup>2</sup> yd <sup>2</sup> mi <sup>2</sup>	square inches	6.5	square centimeters	cm <sup>2</sup>
	square feet	0.09	square meters	m <sup>2</sup>
	square yards	0.8	square meters	m <sup>2</sup>
	square miles	2.6	square kilometers	km <sup>2</sup>
	acres	0.4	hectares	ha
<b>MASS (weight)</b>				
oz lb	ounces	28	grams	g
	pounds	0.45	kilograms	kg
	short tons (2,000 lb)	0.9	tonnes	t
<b>VOLUME</b>				
tsp Tbsp fl oz c pt qt gal ft <sup>3</sup> yd <sup>3</sup>	teaspoons	5	milliliters	ml
	tablespoons	15	milliliters	ml
	fluid ounces	30	milliliters	ml
	cups	0.24	liters	l
	pints	0.47	liters	l
	quarts	0.95	liters	l
	gallons	3.8	liters	l
	cubic feet	0.03	cubic meters	m <sup>3</sup>
	cubic yards	0.76	cubic meters	m <sup>3</sup>
<b>TEMPERATURE (exact)</b>				
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C

\* 1 in. = 2.54 (exactly). For other exact conversions and more detailed tables, see NBS Misc. Publ. 286, Units of Weights and Measures, Price \$2.25, SD Catalog No. C13.10.286.

## Approximate Conversions from Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
mm cm m km	millimeters	0.04	inches	in
	centimeters	0.4	inches	in
	meters	3.3	feet	ft
	kilometers	1.1	yards	yd
		0.6	miles	mi
<b>AREA</b>				
cm <sup>2</sup> m <sup>2</sup> km <sup>2</sup> ha	square centimeters	0.16	square inches	in <sup>2</sup>
	square meters	1.2	square yards	yd <sup>2</sup>
	square kilometers	0.4	square miles	mi <sup>2</sup>
	hectares (10,000 m <sup>2</sup> )	2.5	acres	
<b>MASS (weight)</b>				
g kg t	grams	0.035	ounces	oz
	kilograms	2.2	pounds	lb
	tonnes (1,000 kg)	1.1	short tons	
<b>VOLUME</b>				
ml l l l m <sup>3</sup> m <sup>3</sup>	milliliters	0.03	fluid ounces	fl oz
	liters	2.1	pints	pt
	liters	1.06	quarts	qt
	liters	0.26	gallons	gal
	cubic meters	35	cubic feet	ft <sup>3</sup>
	cubic meters	1.3	cubic yards	yd <sup>3</sup>
<b>TEMPERATURE (exact)</b>				
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F



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The Naval Facilities Engineering Command (NAVFACENGCOM) has tasked the Naval Civil Engineering Laboratory (NCEL) under Work Unit No. 71-058 to investigate ashes generated from incineration of Navy hazardous waste. In many cases, ashes generated are also considered to be hazardous and must be further treated or disposed of as hazardous waste. A technology assessment was also conducted to identify the most appropriate technologies available for treating these ashes and rendering them nonhazardous.

This report is based on one initially written by Roy F. Weston, which addressed incineration and ash treatment technologies. The Weston report was entitled "Evaluation of Thermal and as Treatment Technologies for Navy Hazardous Waste." The thermal treatment portion of this report was eliminated because of questionable relevance to ash treatment technology. In doing so, the report was extensively reorganized with some sections being rewritten, constituting a major revision of the report.

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## LIST OF ACRONYMS

BDAT	- Best demonstrated available technology
DLA	- Defense Logistics Agency
DRE	- Destruction and removal efficiency
DRMO	- Defense reutilization and marketing office
GOCO	- Navy-owned/contractor operated
HSWA	- Hazardous and Solid Waste Amendments of 1984
HW	- Hazardous Waste
HWM	- Hazardous Waste Minimization
IWTP	- Industrial wastewater treatment plant
NADEP	- Naval air depot
NCEL	- Naval Civil Engineering Laboratory
NPDES	- National Pollutant Discharge Elimination System
NSPS	- New Source Performance Standards
NSY	- Naval shipyard
NTIS	- National Technical Information Service
PCB	- Polychlorinated biphenyl
PWD/C	- Public works departments/centers
RCRA	- Resource Conservation and Recovery Act of 1976
R&D	- Research and development
RDT&E	- Research, development, testing, and evaluation
T&E	- Testing and evaluation
TOX	- Total organic halides
U.S. EPA	- United States Environmental Protection Agency

## EXECUTIVE SUMMARY

The Navy, which typically generates several million tons of hazardous waste (HW) each year from its operation and maintenance activities, is currently evaluating new methods of treatment of hazardous wastes (HWs). In calendar year 1985 the Navy generated nearly 4 million tons of HWs that resulted in disposal costs of approximately \$17.2 million. Much of this waste is disposed of in HW landfills. However, regulations promulgated under the Resource Conservation and Recovery Act of 1976 (RCRA) and its amendments have prohibited or will soon prohibit disposal of many untreated wastes in HW landfills.

The Navy recognizes that thermal treatment of HWs should, under the terms of the RCRA, be avoided. Combustion waste disposal may nonetheless become unavoidable in certain cases, even after all possible process enhancements that avoid HW production are implemented. Even then, however, some toxic constituents that may be present in the waste will not be destroyed by incineration and will persist in the ash residue produced by incineration. Such incinerator ash will have to be disposed of in HW landfills. The Navy is thus evaluating methods of treatment of such ash to remove or immobilize the toxic constituents that persist following incineration in order to render the waste treatment residue nonhazardous. Appropriate technology identified in this work can be applied to ash produced by HW combustors operated by the Navy, if any, or be required for ash produced by commercial generators handling Navy HWs.

### Scope

This work was performed under Phase II of Contract No. N62474-87-6-3053 to define the overall ash problems associated with incineration of the Navy's HW. The purpose of this study was to:

- Identify the Navy's highest volume HW streams and determine which of these are possible candidates for incineration after Navy's industrial practices have been modified to achieve optimum HW minimization (HWM).
- Determine the hazardous constituents present in the ashes generated by incinerating representative HWs of the post-RCRA conforming period.
- Identify and evaluate technologies for treatment of hazardous ashes to convert these ashes to a nonhazardous state.

- Design a research, development, testing, and evaluation (RDT&E) program and identify time schedules and funding plans to provide answers to the unresolved problems associated with converting the ashes to a nonhazardous state.

#### Identification of Hazardous Waste Incineration Candidates

The Navy's largest generated HW types and possible candidate wastes for incineration were identified based on a review of the Naval Civil Engineering Laboratory's (NCEL) "Hazardous Waste Minimization Initiation Decision Report"[1]. This report is based on a survey of 23 facilities that produced over 95 percent of the Navy's HW in calendar year 1984.

The single largest waste stream, accounting for 90 percent of the total HW generated in 1985, is treated by Navy industrial wastewater treatment plants (IWTPs) and, after detoxification, is discharged to public sewers or surface water bodies. The other Navy industrial processes produced wastes that represent only 10 percent of the tonnage of HWs but accounted for 58 percent (\$9.9 million) of the Navy's HW disposal costs in calendar year 1985.

An evaluation of the top 17 waste generating processes identified 8 processes with wastes that could not be incinerated because they are either wastewaters treated by Navy IWTPs or are reclaimed, recycled, or redistributed for other uses. Seven of the remaining processes produce 8,639 tons of wastes that are clearly candidates for incineration if they are not eliminated meanwhile. These wastes and the processes from which they are produced are:

- Spent carbon from ordnance operations.
- Sludges from bilge emptying and cleaning (e.g. recovery still bottoms).
- Waste solvents and residues from painting operations and depainting blast media (nonabrasive).
- Waste explosives and propellants from demilitarization.
- Oils and sludges from fluid changeouts.
- Cleaning solvents from maintenance and degreasing operations.
- Solvents and residues from chemical paint stripping (at considerably reduced quantities).

Based on laboratory testing of these wastes, or properties estimated from available literature, incineration could reduce these 8,639 tons of waste to 470 tons of ash, neglecting expected decreases from process enhancements.

### Identification of Hazardous Constituents Present in Incinerator Ash

In order to determine if hazardous constituents are present in the ash from incineration of Navy wastes, samples from five of the nine processes producing wastes that could be incinerated were obtained for laboratory testing. This testing identified that the hazardous constituents that would be present in the ash resulting from incineration of these wastes are primarily heavy metals, such as chromium and cadmium. The results confirmed that ash from the incineration of the HWs would be considered hazardous due to the presence of metals in the EP Toxicity test leachate.

Thermal treatment of heavy metal containing wastes such as IWTP sludge would be beneficial in destroying the toxic organics present, but conventional incineration may actually increase mobility of metals.

The results of this testing also suggest that one of the wastes may not require disposal as a HW. The particular IWTP sludge sample that was tested exhibited low EP Toxicity, indicating that there is a potential for delisting some wastes. Additional testing, including tests for nickel, would be necessary to confirm this for the sludge in question. It is highly improbable, of course, that all IWTP sludge would be so categorized.

### Identification and Evaluation of Ash Treatment Technologies

Since the ash from the incineration of Navy HWs contains toxic constituents, technologies were identified for treatment of the ashes to convert them to a nonhazardous state. Ten technologies with potential for detoxification of ash were identified from a literature search of scientific and engineering databases and a review of existing technologies for treating heavy metal contaminated wastes. These technologies were subject to an evaluation to identify the ash treatment technologies likely to produce product with the lowest EP Toxicity. Based on the technical evaluation, the following three technologies were found to be most promising:

1. Cement/lime pozzolan stabilization.
2. Roasting.
3. Molten glass inclusion.

Two of the three technologies, roasting and molten glass, can be used to treat the original HW directly as well as to treat an ash output from a conventional thermal treatment unit. The third, cement/lime pozzolan stabilization, is solely applicable to ash treatment. The use of a direct waste treatment (or cotreatment) process would result in lower capital equipment cost but possibly higher operating cost as compared to their application in a post-incineration ash treatment process. The decision on which technology to use and whether to employ a cotreatment or posttreatment process scheme should be based on a comparison of performance, operating conditions, and the resultant economics for Navy HWs.

#### Recommendations for RDT&E

In order to address the unknowns associated with treatment/disposal of ash from incineration of the Navy's HWs, the following RDT&E program is recommended:

- Phase 1--Waste Characterization/Source Study

Project future, post-RCRA conformity, Navy waste data needed to provide the basis for RDT&E testing, cost analysis, and future siting (if applicable) assessment.

- Phase 2--Ash Treatment Technology Testing

Bench-scale testing would be conducted on:

- Cement/lime pozzolan stabilization (ash only).
- Roasting with additives (HW and ash).
- Molten glass inclusion (HW and ash).

These test results will provide design parameters and performance data needed to complete an economic/performance analysis of the competing full-scale processes. The resulting recommendation for either an established (i.e., stabilization) or developmental (i.e., roasting or molten glass) process will determine whether pilot testing is necessary.

- Phase 3--Ash Treatment Demonstration

Pilot testing of developmental technologies such as roasting or molten glass to demonstrate these processes should the Phase 2 effort recommend them.

The test plans for the above outlined RDT&E program are presented in Appendix A of this report.

## SECTION 1

### INTRODUCTION

The Navy typically generates several million tons of hazardous waste (HW) each year from its operation and maintenance activities. In calendar year 1985 the Navy generated nearly 4 million tons of HW that resulted in disposal costs of approximately \$17.2 million. Much of this waste is disposed of by landfilling; however, regulations promulgated under the Resource Conservation and Recovery Act of 1976 (RCRA) and the Hazardous and Solid Waste Amendments of 1984 (HSWA) will eventually prohibit land disposal of most untreated HW [2, 3]. Therefore, the Navy is evaluating new methods of treatment of HWs. The approach has been to avoid the production of HWs through modification of the industrial processes practiced at Navy activities. The goal is, thus, to shut down the pipeline that produces HWs that might otherwise have to be disposed of by incineration and/or burial.

While the Navy recognizes that thermal treatment of HWs should, under the terms of the RCRA, be avoided, it may nonetheless become unavoidable in certain cases, even after process enhancements are implemented. In order for the ash residue generated from the incineration of HW to be considered nonhazardous, the hazardous constituents of the waste must be destroyed or rendered immobile. Constituents that make wastes hazardous include organic and inorganic compounds. Incineration is effective in destroying the organic (carbon-based) constituents of HW and reducing the volume of the waste. However, inorganic constituents in the waste, such as toxic heavy metals, are not destroyed and will be present in the ash residue remaining after thermal treatment of the waste.

This study, conducted under Phase II of Contract No. N62474-87-6-3053, is part of the Navy's research and development (R&D) effort to define the overall problems associated with the Navy's HW. It includes an evaluation of thermal treatment technologies and technologies that can be applied to render metals-laden ash nonhazardous. This report also recommends a program for research, development, testing, and evaluation (RDT&E) necessary to solve the problems associated with disposal of the Navy's HW via incineration, either on Navy sites or those of commercial operators.



## 1.1 PROJECT SCOPE

Thirty thermal treatment technologies were identified by a literature review and presented in "Evaluation of Infrared and Other Thermal Treatment Technologies for Hazardous Waste," [4] under Phase I of Contract No. N62474-87-6-3053.

The objectives of this work, conducted under Phase II of the contract, were to project future industrial process trends to HWM and to:

- Review the Navy's largest generated HW streams, and select possible future HWs for incineration.
- Determine, predict, or estimate the characteristics of the ashes that will be generated by incinerating the selected future Navy HWs.
- Identify the constituents that might render these ashes hazardous.
- Identify and evaluate technologies for treatment of hazardous ashes to convert these ashes to a non-hazardous state. Determine what R&D efforts are necessary to implement the most appropriate ash treatment technology(ies).

Following NAVFAC review of this report and concurrence with the recommendations presented, NCEL will develop a testing and evaluation (T&E) program to provide answers to the unresolved problems associated with the treatment of the ash residue remaining after incineration.

In order to meet these objectives, the following tasks were undertaken:

- Review of the Navy's "Hazardous Waste Minimization Initiation Decision Report" [1] to identify the Navy HWs that account for a significant fraction of the HW burden and will continue to be produced at some levels despite the HWM program aimed at their reduction.
- Evaluation of these future Navy HWs for incineration by the thermal treatment technologies identified during Phase I of the project.
- Laboratory testing of representative samples of Navy's HWs to determine:
  - The effectiveness of thermal treatment in destroying the hazardous constituents present in these wastes.

- The hazardous constituents present in the ash residue produced by incineration of these wastes.
- Identification of the best choice technologies for treatment of hazardous constituents present in the ash residue.
- Identification of regulatory requirements pertinent to thermal treatment and residue management for the Navy's HW.

## 1.2 REPORT ORGANIZATION

This report presents the results of work completed under Phase II of the contract. The report is organized into five sections as follows:

- Section 1 of this report discusses the purpose and scope of this project.
- Section 2 reviews the principal Navy HW streams and selects nine to evaluate for thermal treatment. It also considers the regulatory requirements relevant to their disposal.
- Section 3 presents the results of laboratory tests to identify the hazardous constituents present in representative samples of the Navy's HW and ash generated from these wastes in laboratory studies. This section also presents an overview of the chemical phenomena that occur in an incinerator that causes ash residues to be hazardous. Regulations pertinent to disposal of these ashes are also discussed.
- Section 4 of this report evaluates 10 technologies identified as potentially applicable for treatment of the ashes generated from incineration of the Navy's HW. The best choice technologies are selected and compared.

## SECTION 2

### NAVY HAZARDOUS WASTES

Information on HW generated by the Navy was reviewed to identify the highest volume waste streams that may be suitable for incineration. In addition, the present and impending land disposal bans on certain hazardous wastes were reviewed to determine which wastes must be treated prior to disposal.

This section of the report:

- Presents an overview of the magnitude of HWs generated by the Navy and the costs associated with their disposal.
- Reviews available information on the highest volume Navy HWs and identifies nine high volume wastes that are potential candidates for thermal treatment.
- Discusses the physical and chemical characteristics of these wastes as they pertain to their thermal treatability.
- Presents RCRA regulations on the disposal of these wastes and the ash residue that remains after thermal treatment.

The primary data source provided by the Navy was a comprehensive survey performed by the Naval Civil Engineering Laboratory (NCEL) [1] that identified the major HWs generated by Navy industrial processes in calendar year 1985. Generators included:

- Naval shipyards (NSYs).
- Naval air depots (NADEPs).
- Public works departments/centers (PWD/Cs).
- Marine Corps activities.
- Navy-owned/contractor-operated (GOCOs).

## 2.1 HAZARDOUS WASTE GENERATED BY NAVY PROCESSES

In calendar year 1985, the Navy generated nearly 4 million tons of HW that resulted in disposal costs of approximately \$17.2 million. Table 2-1 summarizes the wastes, ranked according to quantity (in excess of 5 ton/yr), generated by 32 different industrial processes operating at one or more of 23 Naval facilities. Not all processes are present or operational at all of the facilities. Asbestos and polychlorinated biphenyls (PCBs), considered special action items, are excluded from the evaluation. Detailed information and references on 17 of the highest quantity waste generating processes are presented in "Hazardous Waste Minimization Initiation Decision Report" [1].

At many Naval facilities, the industrial wastewater treatment plant (IWTP) receives aqueous waste streams contaminated with organics and metals discharged from manufacturing/maintenance processes and acts as the final onsite waste treatment step. The large quantity of waste from the IWTP and electroplating/metal finishing processes is actually wastewaters that are treated at IWTPs and discharged under NPDES permits. The IWTP itself generates sludges and residues requiring treatment or disposal, the most notable of these being the metal hydroxide and lime/alum sludges generated as a result of treatment of wastes generated by the electroplating processes. A number of other waste-generating processes are interrelated, such as chemical paint stripping performed prior to painting and metal preparation and solvent cleaning performed prior to electroplating.

The top 17 waste generating processes presented in Table 2-1 account for over 99 percent of the Navy's HW. From these 17 waste generating processes, nine waste streams were identified as potential candidates for thermal treatment. The others were not considered further because they are either routed to the IWTP for treatment or are reclaimed, recycled, or otherwise redistributed for other uses. The rationale for elimination of the other waste streams is summarized as follows:

- Electroplating/metal finishing wastewaters are treated by an IWTP or offsite contractor.
- Pipe flushing/cleaning solvents and solutions are either recycled or treated by an IWTP. Several naval facilities also use offsite treatment.
- Boiler layup operations wastewaters are treated by an IWTP, sewage treatment plant (STP), or offsite contractors.

Table 2-1

Navy Hazardous Waste Generating Processes Ranked by  
Annual Tonnage of Wastewater and Hazardous Wastes

Waste ID	Process ID	Tons	Cost (\$)
1	Industrial Wastewater Treatment Plant (IWTP)	3,680,533	7,357,545
2	Electroplating/Metal Finishing	235,191	978,596
3	Ordnance	26,738	NR
4	Bilge Water Processing	12,473	691,260
5	Abrasive Blasting	6,662	899,815
6	Painting Operations	4,139	1,533,612
7	Demilitarization	3,649	NR
8	Pipe Flushing/Cleaning	3,432	508,970
9	Boiler Lay-up	3,122	55,560
10	Ship Boiler Cleaning	3,019	287,520
11	Fluids Changeout	2,681	630,332
12	Submarine Steam Generator Cleaning	1,555	372,695
13	Solvent Cleaning	1,336	357,915
14	Battery Repair/Replacement	1,268	992,355
15	Metal Prep	1,081	178,418
16	Bilge Derusting	1,045	506,975
17	Chemical Paint Stripping	904	447,350
18	Torpedo Cleaning	683	134,780
19	Vehicle Wash/Repair	440	59,850
20	Bilge/Tank Cleaning	350	58,000
21	Firefighting Practice	258	17,568
22	Container/Drum Disposal	202	468,900
23	Breathing Apparatus	182	368,995
24	Chem Lab	170	34,000
25	Tank Cleaning - CHT System	170	NR
26	Fueling Operations	158	126,250
27	Bilge/Tank Degreasing	120	3,025
28	Air Conditioner Repair	109	46,440
29	Ships Offloaded Stores	85	50,150
30	Boiler Testing	54	21,350
31	L.E.S.S. Manufacturing	52	4,175
32	Fluorescent Tube Replacement	47	8,977
TOTAL		3,997,922 <sup>a</sup>	\$17,201,378

Notes: NR = Not reported.

<sup>a</sup> Includes nonrecurring wastes such as spill cleanup or accumulation of out-of-spec fuels that do not intrinsically involve ongoing practices or processes. These account for 6,014 ton/yr with no reported disposal cost.

- Boiler cleaning wastewaters are treated by an IWTP, STP, or offsite contractors.
- Submarine steam generator cleanout wastewaters are treated by the IWTP or offsite contractors.
- Battery repair and replacement wastes have several treatment options. Battery casings are disposed of in nonhazardous waste landfills. Lead plates are sent to a battery reclaimer. Spent electrolyte is either reclaimed, recycled, or neutralized at an IWTP.
- Metal Preparation waste acids and alkalis are treated by an IWTP or offsite contractor.
- Bilge derusting wastewaters are treated by an IWTP or offsite contractor.

The nine high volume HWS that may be suitable for incineration include:

- IWTP sludge.
- Spent carbon from ordnance operations.
- Bilge emptying and cleaning wastes.
- Abrasive blasting residues.
- Waste solvents and paint residues from painting operations.
- Waste explosives/propellants from munitions demilitarization.
- Oils and sludges from fluids changeout.
- Cleaning solvents.
- Chemical paint stripping solvents and residues.

These wastes fall into four general categories based on chemical composition:

- Chlorinated organics.
- Nonchlorinated organics.
- Metal hydroxide sludges.

- Inorganic (lime/alum) sludges with possible metals contamination.

Ignitable, reactive, or hazardous/toxic organic compounds can be effectively destroyed by thermal treatment under the proper conditions. In some cases under current regulations, the U.S. Environmental Protection Agency (U.S. EPA) may call for the use of thermal treatment even when the level of toxic/hazardous constituents and the fuel value are low. Thus, while wastes such as IWTP sludge and abrasive blasting residues are not typically considered suitable for incineration, they are included here because of the presence of low levels of toxic/hazardous organics and, as will be described later in the report, in the event that thermal treatment for organics and metals proves to be feasible.

Table 2-2 presents reported or estimated information on the physical form, ash content, metals content, and heating value of the wastes. Evaluation of these parameters is important when considering these wastes for incineration.

The physical form (solid, liquid, sludge) of the waste determines the type of waste feeding mechanism required. The physical form of the waste may also preclude the use of a specific thermal destruction technology because many technologies can treat only specific forms of waste (e.g., liquid incineration can treat only liquids).

The ash content of the waste provides an estimate of the volume of ash residue that remains after incineration. Since ash generated from the incineration of HWs is still considered a HW under U.S. EPA regulations, wastes that have a high ash content will have greater ash treatment and disposal requirements.

Metals present in the waste will be present in the ash residue that remains after incineration because metals are not destroyed by incineration. For this reason, wastes with high metals content are typically not considered good candidates for incineration. However, the presence of toxic organic compounds in these wastes may justify consideration of the waste for incineration.

The heating value of the waste provides an indication of whether additional fuel will be necessary to incinerate the waste. Wastes having low heating values will require the co-firing of supplemental fuel to maintain the high temperatures needed for thermal destruction.

Table 2-2

Nine Principal Potentially Incineratable Navy Hazardous Wastes<sup>a</sup>

ID No.	Process or Waste	Physical Form	Organic Constituents			Estimated		
			Halogenated (%)	Nonhalogenated (%)	Ash Content (%)	Metals (%)	Water Content (%)	Heating Value (Btu/lb)
1	IWTP Sludge	Sludge	<10	<10	160	10 to 60	10 to 60	<5,000
3	Spent Carbon from Ordnance Operations	Solid	<10	160	<10	<10	<10	15,000
4	Bilge Emptying and Cleaning Waste	Sludge	<10	10 to 60	<10	<10	10 to 100	15,000
5	Abrasive Blasting Residues	Sludge	<10	<10	160	10 to 60	<10	<5,000
6	Waste Solvents and Paint Residues from Painting Operations	Liquid, Solid, and Sludge	160	160	<10	<10	10 to 60	<5,000
7	Waste Explosives/Propellants and Ash from Munitions Demilitarization	Solid	<10	160	10 to 60	<10	<10	15,000

Notes:

<sup>a</sup>Hazardous Waste Minimization IDR (NCEL, internal document).<sup>b</sup>Indicates if auxiliary combustion fuel is required for incineration. Wastes with heating values less than 5,000 Btu/lb generally require auxiliary fuel.



Table 2-2  
(continued)

ID No.	Process or Waste	Physical Form	Organic Constituents		Estimated			
			Halogenated (%)	Nonhalogenated (%)	Ash Content (%)	Metals (%)	Water Content (%)	Heating Value (Btu/lb)
11	Oils and Sludges from Fluids Changeout	Liquid and Solid	160	160	<10	10 to 60	<10	15,000
13	Cleaning Solvents	Liquid	160	160	<10	10 to 60	<10	<5,000
17	Chemical Paint Stripping Solvents and Residues	Liquid and Solid	10 to 100	10 to 100	<10	10 to 60	<10	<5,000

Notes:

<sup>a</sup>Hazardous Waste Minimization IDR (NCEL, internal document).

<sup>b</sup>Indicates if auxiliary combustion fuel is required for incineration. Wastes with heating values less than 5,000 Btu/lb generally require auxiliary fuel.

Table 2-3 summarizes the waste quantities for the waste streams that are clearly incineratable or that require thermal treatment as well as those that are not normally considered incineratable but for which thermal treatment would potentially be required or beneficial (i.e., organic/metal cotreatment). According to 1985 data, 8,639 ton/yr of high volume Navy wastes are clearly incineratable, and an additional 13,804 ton/yr are potentially incineratable.

## 2.2 REGULATORY REQUIREMENTS

One of the most significant aspects of the 1984 amendments to RCRA is the land disposal restrictions or land ban. The 1984 amendments prohibit the disposal of certain untreated HWs in HW landfills unless these wastes are treated to standards established by the U.S. EPA. Wastes that meet the treatment standards may be disposed of in HW landfills.

Navy industrial processes generated several of the wastes that are prohibited from land disposal. Of the nine Navy HWs presented in Table 2-2, the following five are prohibited from land disposal:

- Waste ID 1: IWTP sludge (U.S. EPA Hazardous Waste ID F006).
- Waste ID 3: Spent carbon from ordnance operations (U.S. EPA Hazardous Waste ID K045).
- Waste ID 6: Waste solvents and paint residues from painting operations (U.S. EPA Hazardous Waste IDs F001 through F005).
- Waste ID 13: Cleaning solvents (U.S. EPA Hazardous Waste IDs F001 through F005).
- Waste ID 17: Chemical paint stripping solvents and residues (U.S. EPA Hazardous Waste IDs F001 through F005).

In order to dispose of these land banned wastes, they must be treated to the best demonstrated available technology (BDAT) treatment standards established by the U.S. EPA. BDAT treatment standards for these wastes are presented in Table 2-4.

An understanding of how the BDAT treatment standards were established provides insight into the level of treatment required before these wastes can be land disposed. The U.S. EPA established the BDAT treatment standards by evaluating the best available technologies for treatment of the wastes prohibited from land disposal. Because thermal technologies are effective

Table 2-3

## Summary of Clearly/Potentially Incineratable Wastes

ID Number	Process or Waste	U.S. EPA Hazardous Waste ID Number <sup>a</sup>	Quantity <sup>b</sup> (ton/yr)	Disposal Costs <sup>b</sup> (\$1,000/yr)
CLEARLY INCINERATABLE:				
3	Spent Carbon from Ordnance Operations	K044	33 <sup>c</sup>	NR
4	Bilge Emptying and Cleaning Waste	NA <sup>d</sup>	312 <sup>e</sup>	691 <sup>f</sup>
6	Waste Solvents and Paint Residue from Painting Operations	D001, D004, D011 F001-F003, F005	530 <sup>g</sup>	NR
7	Waste Explosives/ Propellents from Munitions Demilitarization	D003	3,649 <sup>h</sup>	NR
11	Oils and Sludges from Fluids Changeout	D001, D002, F001, F002	2,681	630
13	Cleaning Solvents	F001-F003, F005, D001	530 <sup>i</sup>	NR
17	Chemical Paint Stripping Solvents and Residues	F001-F005 D001, D002, D004 D006-D008, D010, D011	<u>904</u>	<u>447</u>
SUBTOTAL			8,639	>1,768
POTENTIALLY INCINERATABLE:				
1	Industrial Wastewater Treatment Plant Sludge	F006	7,142 <sup>j</sup>	1,384 <sup>k</sup>
5	Abrasive Blasting		<u>6,662</u>	<u>900</u>
SUBTOTAL			<u>13,804</u>	<u>2,284</u>
TOTAL			22,443	4,052

See notes on following page.

NOTES:

NA = Not applicable.

NR = Not reported.

<sup>a</sup>Waste may include, but is not limited to, these U.S. EPA Hazardous Waste Identification Numbers [5,6].

<sup>b</sup>Based on 1985 quantities and costs [1].

<sup>c</sup>Based on 0.04 percent explosive compounds in wastewater adsorbed onto carbon at a ratio of 0.32 lb explosives/1.0 lb carbon [7,8].

<sup>d</sup>This waste may not be defined as a hazardous waste under U.S. EPA regulations. However, some states classify oily wastes as hazardous, and the U.S. EPA may eventually follow their lead.

<sup>e</sup>Represents annual quantity of oily sludges. Excludes 12,161 tons of wastewater that are discharged to a publicly owned treatment works plant (POTWP) or surface water body under a National Pollution Discharge Elimination System (NPDES) permit. Based on a worst-case oily sludge production rate equal to 2.5 percent of the oily wastewater processed [9].

<sup>f</sup>Includes costs for recycling recovered oil, wastewater treatment, and sludge disposal. Itemized costs are not available [10].

<sup>g</sup>Represents annual quantity of waste solvents. Excludes wastewater, dry paint filters, and paint sludges that are not itemized and account for 3,609 ton/yr [11]. Dry paint filters and dewatered paint sludge may also be potentially incineratable.

<sup>h</sup>Probably high estimate.

<sup>i</sup>Represents annual quantity of waste solvents disposed of. Excludes solvent still bottoms and solvents recycled under the Used Solvent Elimination (USE) program that are not itemized and account for 806 ton/yr [12].

<sup>j</sup>Represents annual quantity of sludges. Excludes 3,673,391 tons of wastewater that are discharged to POTWP or surface water bodies under an NPDES permit [13].

<sup>k</sup>Represents annual cost for sludge disposal. Excludes \$5,973,170/yr for IWTP operations [13].

Table 2-4

BDAT Treatment Standards

a. BDAT Treatment Standards for F006 Nonwastewaters

Constituent	Maximum Concentration in TCLP Leachate for Any Single Grab Sample (mg/L)
Cadmium	0.066
Chromium (total)	5.2
Lead	0.51
Nickel	0.32
Silver	0.072

Source: [14].

b. BDAT Treatment Standards for K045 Nonwastewaters

The final treatment standard for K045 is no land disposal. EPA does not consider open burning and open detonation of reactive (e.g., explosive) wastes to be land disposal as long as no reactive constituents remain after detonation.

Source: [14].

c. BDAT Treatment Standards for F001-F005 Spent Solvents

F001-F005 Spent Solvents	Concentration (mg/L)	
	Wastewaters Containing Spent Solvents	All other Spent Solvent Wastes
Acetone	0.05	0.59
n-Butyl alcohol	5.0	5.0
Carbon disulfide	1.05	4.81
Carbon tetrachloride	.05	.96
Chlorobenzene	.15	.05
Cresols (and cresylic acid)	2.82	.75
Cyclohexanone	.125	.75
1,2-Dichlorobenzene	.65	.125
Ethyl acetate	.05	.75
Ethylbenzene	.05	.053
Ethyl ether	.05	.75
Isobutanol	5.0	5.0
Methanol	.25	.75
Methylene chloride	.20	.96
Methylene chloride (from the pharmaceutical industry)	12.7	.96
Methyl ethyl ketone	0.05	0.75
Methyl isobutyl ketone	0.05	0.33
Nitrobenzene	0.66	0.125
Pyridine	1.12	0.33
Tetrachloroethylene	0.079	0.05
Toluene	1.12	0.33
1,1,1-Trichloroethane	1.05	0.41
1,1,2-Trichloro-1,2,2-trifluoroethane	1.05	0.96
Trichloroethylene	0.062	0.091
Trichlorofluoromethane	0.05	0.96
Xylene	0.05	0.15

Source: [15].

for treating many organic wastes, the residual concentrations of organic compounds present in the ash from incineration of these wastes has been established as the BDAT standard for many organic wastes. The BDAT treatment standards are regulatory requirements that a waste must meet to be disposed of in a HW landfill. The use of BDAT to achieve these standards is not a regulatory requirement, although it may be the only technology currently capable of meeting these standards. Consequently, to dispose of a HW such as Navy cleaning solvents (U.S. EPA Hazardous Waste IDs F001F005) that do not meet the BDAT standards, the waste must be incinerated and shown to contain concentrations less than the BDAT standards for the ash to be disposed of in a HW landfill. Thus, for many of the nine Navy HWs identified, thermal treatment is not only appropriate but is the regulatory choice for meeting the BDAT requirements.

## SECTION 3

### WASTE AND ASH CHARACTERIZATION

Ash residues from the incineration of hazardous waste (HW) typically remain HW and have historically been landfilled. It may be necessary to treat these wastes to render them nonhazardous in order to meet future land ban restrictions.

The characteristics of ash from the nine selected Navy wastes were evaluated to provide a basis for identifying ash treatment technologies and objectives. This section of the report:

- Describes the fate of heavy metals in incinerators.
- Presents the results of laboratory analysis of five of the nine selected Navy HWs and their ashes.
- Presents the regulatory requirements for ash treatment and disposal.

#### 3.1 FATE OF HEAVY METALS IN INCINERATORS

Hazardous wastes consist of hazardous organic and inorganic constituents. Thermal destruction of HW in a RCRA-permitted combustor must be effective in destroying 99.99% of the organic constituents present in the waste while reducing the volume of waste. Inorganic constituents such as toxic heavy metals present in the waste are not destroyed. Heavy metals typically can be present in four streams from incineration:

- Combustion gases.
- Fly ash.
- Bottom ash.
- Wastewater from gas scrubbing/absorption.



The distribution of metals in these streams depends on the chemical composition of the waste and the operating conditions of the incinerator. Due to the complexities of combustion chemistry, the distribution of metals is difficult to predict. However, the following general statements regarding the fate of heavy metals in an incinerator can be made:

- Metal forms with relatively low melting temperatures and/or that vaporize directly from the solid (sublime) will predominate in the fly ash and combustion gases.
- Metal forms with higher boiling temperatures will predominate in the bottom ash.
- Metals may be distributed based on the melting temperatures of their oxides if the incinerator is operated under oxidizing (oxygen-rich) conditions.
- The presence of halogens in the waste promotes metal halide formation, which increases vaporization of metals and their concentration in the fly ash.

Metal forms that have low melting points or that sublime at relatively low incineration temperatures (less than 1,500°F) tend to vaporize into the combustion gases. For example, given an equal concentration of lead and chromium in a waste, lead should vaporize to the combustion gases at a higher rate because its melting temperature (621°F) is lower than that of chromium (3,407°F). Metals that vaporize into the combustion gases may be removed as particulates by air cooling, condensation, and filtering using pollution control equipment. However, some metals may still be emitted to the atmosphere for two reasons:

- A fraction of the metals may be present as particulates less than 1 micron in diameter. Particles smaller than this size are difficult to remove with air pollution control equipment and will not precipitate from the flue gas.
- Metals with very low melting temperatures, such as mercury, which is a liquid at room temperature, may remain in vapor form.

In contrast, metals with high melting temperatures will predominate in the bottom ash. Using the example of lead (melting temperature 621°F) and chromium (melting temperature 3,407°F), chromium would be expected to predominate in the bottom ash.

Operation of the incinerator under oxidizing (oxygen-rich) conditions is necessary for organic destruction but may promote the formation of metal oxides. These oxides would be distributed between the fly ash and bottom ash based on the melting temperatures of the oxides. For example, elemental chromium (melting temperature 3,407°F) would be expected to remain in the bottom ash while one of its oxides,  $\text{CrO}_3$  (melting temperature 385°F), would be expected to be in the fly ash. However, most metal oxides are less volatile than their elemental forms. As an example, another oxide of chromium,  $\text{Cr}_2\text{O}_3$  (melting temperature 4,415°F), is less volatile than the elemental metal and would also remain in the bottom ash.

The presence of halogens in the waste will affect the distribution of metals in the fly ash and bottom ash. Halogens in the waste lead to the formation of metal halides in the incinerator. Generally, metal halides have lower melting temperatures than the metal itself, as is demonstrated by the chromium chlorides. Chromium dichloride,  $\text{CrCl}_2$ , has a melting temperature of 1,500°F compared with the melting temperature of 3,407°F for elemental chromium. Chromium trichloride,  $\text{CrCl}_3$ , vaporizes directly from the solid (sublimes) at 1,733°F. Since some of the metal halogens may escape air pollution control equipment, it may be advantageous to segregate halogenated wastes and heavy metal wastes, where possible.

Metals may also be present in the effluent from scrubbing or adsorption equipment used for air pollution control. The pH of the effluent is typically adjusted and discharged or, if small enough in volume, recycled to the incinerator for ash cooling.

Clearly, the phenomena governing the distribution of metals in incinerator residues are complex. The chemical composition of the wastes and incinerator operating conditions both affect the distribution of heavy metals in the fly and bottom ash. Since ash composition is dependent on the composition of the waste and complex, high-temperature chemical reactions, several samples of Navy wastes were obtained for laboratory analysis and incineration. The next subsection of this report describes the experimental program.

### 3.2 WASTE AND ASH CHARACTERIZATION

In order to determine the hazardous organic and inorganic constituents present in Navy wastes and the ash residue from thermal treatment of these wastes, NCEL provided representative samples of five Navy waste streams. These samples were obtained from the following operations or processes and are identified by the sample identification numbers indicated:

- IWTP sludge (WS-1).
- Bilge emptying and cleaning sludge (WS-4).
- Painting operations sludge (WS-6).
- Fluids changeout (WS-11).
- Cleaning solvents (WS-13).

With the exception of the bilge emptying and cleaning sludge, all samples were collected at the Norfolk Naval Aviation Depot in Norfolk, Virginia. Bilge emptying and cleaning sludge was collected at the Craney Island Fuel Depot, Craney Island, Virginia.

### 3.2.1 Procedure

Samples were analyzed by WESTON Analytics, Lionville, Pennsylvania, for the parameters indicated in Table 3-1. Portions of the waste samples were retained for ashing by ASTM Method D3174 at 1,382°F. Ashing was performed by WESTON's Environmental Testing Laboratory (ETL) in Lionville Pennsylvania, and Fuller Company of Bethlehem, Pennsylvania. Samples of ash were analyzed for the parameters indicated in Table 3-1. Due to low ash content of the fluids changeout waste (WS-11), sufficient ash could not be generated for laboratory analysis. Multiple samples of this waste were collected in an attempt to generate sufficient ash; however, due to project time constraints, sufficient ash could not be generated for laboratory analysis.

### 3.2.2 Results of Waste Characterization

Table 3-2 presents the results of analysis of waste samples for various chemical and physical properties. Results of particular importance are the following:

- The heating value of most of the wastes is very low. Incineration of wastes with a heat of combustion less than 5,000 Btu/lb generally requires auxiliary fuel [20], for a RCRA-permitted combustor, fuel value of the waste would be of no importance.
- Organic halides were present in wastes from painting operations (WS-6), fluids changeout (WS-11), and solvent cleaning (WS-13). Combustion of halogenated wastes creates acid gases requiring acid-gas scrubbing as part of the emissions control system.

Table 3-1

## Summary of Analyses Performed on Waste and Ash Samples

Analytical Parameter	Waste	Ash
Pesticides/PCBs	X	X
Volatile Organic Compounds	X	X
Semivolatile Organic Compounds	X	X
Metals, EP Toxic	X	X
Metals, Total RCRA	X	
Dioxin/Furans	X	
Miscellaneous Chemical/Physical Properties		
Oxidation Potential	X	
Ignitability	X	
Corrosivity	X	
% Ash	X	
% Solids	X	
Heat of Combustion	X	
Density	X	
pH	X	
Cyanide, total	X	
Phenol	X	
Sulfide	X	
Total Organic Halides (TOX)	X	

Table 3-2

# Results of Miscellaneous Physical/Chemical Analyses of Waste Samples

Analytical Parameter	IWTP Sludge		Bilge Emptying Sludge		Painting Operations		Fluids Changeout		Cleaning Solvents	
	Raw	Waste	Raw	Waste	Raw	Waste	Raw	Waste	Raw	Waste
	WS-1	WS-1	WS-4	WS-4	WS-6	WS-11	WS-11	WS-13		
Misc. Chemical/Physical Properties										
Oxidation Potential	Negative	Negative	Negative	Negative	Negative	Negative	Negative	Negative	Negative	Negative
Ignitability	39.1	40.3	6.5	15	12.4	39.4	0.87	94.6	33.9	72.9
% Ash	ND	ND	Not Ignitable	Not Ignitable	4560	ND	18300	ND	Not Ignitable	Not Ignitable
% Solids	1.1	12.4	0.98	7.3	1.2	9.6	0.87	3.3	1.2	13
Heat of Combustion (BTU/lb)	23.8	39.5	ND	ND	ND	ND	ND	ND	0.862	1.14
Corrosivity (mm/yr)	ND	ND	56.3	ND	9920	ND	22.4	0.1	ND	ND
Density (g/cc)	ND	ND	ND	ND	24000	ND	500	12000		
pH										
Cyanide, Total (ppm)										
Phenol (ppm)										
Sulfide (ppm)										
TOX, Total Organic Halides (ppm)										

NOTES: ND = Not Detected

- The IWTP sludges (WS-1) had high ash content due to the high concentration of nonincineratable compounds, such as calcium, in this waste.

Table 3-3 presents the results of analyses of waste and ash samples for organic compounds (pesticide/PCBs, volatile organic compounds, semivolatile organic compounds). The results of waste analysis indicate the following:

- The painting operations (WS-6) and fluids changeout (WS-11) wastes contained the pesticides Beta-BHC and Endosulfan II. The reason for the presence of these pesticides in these samples could not be determined.
- All of the wastes contained some form of hazardous chlorinated or nonchlorinated volatile organic compounds. The presence of chlorinated volatile organic compounds such as 1,1,1-trichloroethane, trichloroethene, and tetrachloroethene in the wastes indicates that acid gases will be generated during incineration of these wastes and that acid gas scrubbing will be required as part of the emissions control system.
- Hazardous semivolatile organic compounds were present in all of the wastes, especially the waste from painting operations (WS-6). The presence of these compounds in these wastes was expected.

Table 3-4 presents the results of analyses of waste and ash samples for heavy metals. Wastes were analyzed for total heavy metals and Extraction Procedure (EP) leachable heavy metals. Analysis for total metals gives the total concentration metals present in the waste feed that may be subject to the complex interactions described in Subsection 3.1. Analysis for EP leachable metals provides a measure of the rate of metals leaching from the waste, which is one criterion for determining if the waste is hazardous.

The results of total metals analysis indicate that all of the wastes contain heavy metals. As would be expected, the concentrations of these metals are greatest in the IWTP sludge (WS-1) and painting operations waste (WS-6). The principal metals present are cadmium, chromium, and lead.

The results of EP leachate from these wastes indicate the following:

- The metals present in the IWTP sludge (WS-1) did not leach from the raw waste.

Table 3-3

Results of Organic Analyses of  
Waste and Ash Samples

Analytical Parameter	IWTP Sludge		Bilge Emptying Sludge		Painting Operations		Fluids Changeout		Cleaning Solvents	
	Raw Waste WS-1 (ppb)	Ash WS-1A (ppb)	Raw Waste WS-4 (ppb)	Ash WS-4A (ppb)	Raw Waste WS-6 (ppb)	Ash WS-6A (ppb)	Raw Waste WS-11 (ppb)	Ash WS-11A (ppb)	Raw Waste WS-13 (ppb)	Ash WS-13A (ppb)
Pesticides/PCBs										
Beta-BHC	ND	ND	ND	ND	420 J	ND	ND	NA/IS	ND	ND
Endosulfan II	ND	ND	ND	ND	ND	ND	12000 J	NA/IS	ND	ND
Volatile Organic Compounds										
Chloroform	7 J	ND	ND	2 J	ND	2 J	ND	NA/IS	ND	ND
2-Butanone	ND	ND	ND	ND	ND	15	31000	NA/IS	ND	ND
1,1,1-Trichloroethane	24	ND	ND	6	ND	ND	9700	NA/IS	ND	ND
Trichloroethene	ND	ND	28000 J	ND	2700000	ND	ND	NA/IS	ND	ND
Benzene	ND	ND	ND	ND	ND	ND	8700	NA/IS	ND	ND
4-Methyl-2-pentanone	ND	ND	ND	ND	ND	ND	12000 J	NA/IS	77	ND
2-Hexanone	ND	ND	ND	ND	ND	2 J	ND	NA/IS	ND	ND
Tetrachloroethene	22	ND	ND	ND	1600000	ND	ND	NA/IS	ND	ND
Toluene	10 J	3 J	31000 J	62	530000	16	640000	NA/IS	30	ND
Ethylbenzene	ND	ND	ND	ND	ND	1 J	ND	NA/IS	ND	ND
Styrene	60	ND	ND	ND	ND	ND	ND	NA/IS	ND	ND
Total Xylenes	ND	ND	ND	ND	ND	8	180000 B	NA/IS	ND	ND
Semivolatile Organic Compounds										
Phenol	4100	ND	ND	ND	3400000	ND	ND	NA/IS	2500 J	ND
1,3-Dichlorobenzene	ND	ND	ND	ND	5000000	ND	ND	NA/IS	ND	ND
1,4-Dichlorobenzene	ND	ND	ND	ND	9400000	ND	ND	NA/IS	ND	ND
1,2-Dichlorobenzene	5500	ND	ND	ND	192000000	ND	ND	NA/IS	ND	ND
4-Methylphenol	ND	ND	ND	ND	ND	ND	ND	NA/IS	1200 J	ND
Isophorone	ND	1400	ND	ND	1300000 J	ND	ND	NA/IS	ND	ND
2,4-Dimethylphenol	ND	ND	ND	ND	ND	57 J	ND	NA/IS	ND	ND
Naphthalene	610 J	ND	ND	ND	ND	ND	ND	NA/IS	ND	ND
2-Methylnaphthalene	1800 J	ND	62000 J	ND	ND	ND	120000 J	NA/IS	ND	ND
Phenanthrene	2500 J	ND	ND	ND	ND	ND	ND	NA/IS	ND	ND
Di-n-Butylphthalate	ND	120 J	ND	ND	ND	86 J	ND	NA/IS	ND	52 J
bis (2-Ethylhexyl) Phthalate	11000	210 J	ND	ND	ND	ND	ND	NA/IS	ND	ND
Dioxin/Furans										
Octachlorinated Dibenzodioxin	ND	NR	1.1	NR	ND	NR	5	NR	ND	NR
Heptachlorinated Dibenzofuran	ND	NR	ND	NR	ND	NR	4	NR	ND	NR
Octachlorinated Dibenzofuran	ND	NR	ND	NR	ND	NR	4	NR	ND	NR

NOTES: J = Indicates an estimated value. This flag is used when the concentration in the sample is outside the instrument calibration range or the identity of the compound is tentative.

ND = Not Detected

NR = Analysis for this parameter was not requested.

NA = Not Analyzed.

NA/IS = Not Analyzed. Insufficient sample was available for analysis.

Table 3-4

# Results of Chemical Inorganic Analyses of Waste and Ash Samples

Analytical Parameter	IWTP Sludge		Sludge Emptying Sludge		Painting Operations		Fluids Changeout		Cleaning Solvents	
	Raw Waste WS-1 (ppm)	Ash WS-1A (ppm)	Raw Waste WS-4 (ppm)	Ash WS-4A (ppm)	Raw Waste WS-6 (ppm)	Ash WS-6A (ppm)	Raw Waste WS-11 (ppm)	Ash WS-11A (ppm)	Raw Waste WS-13 (ppm)	Ash WS-13A (ppm)
Metals, EP Leachate										
Silver	ND	ND	ND/ND	ND	ND	ND	NA/LIQ	NA/IS	ND	ND
Barium	ND	1.11	ND/ND	ND	ND	ND	NA/LIQ	NA/IS	ND	ND
Cadmium	ND	ND	ND/ND	0.426	1.61	7.18	NA/LIQ	NA/IS	19.4	ND
Chromium	ND	17.5	ND/0.177	ND	ND	ND	NA/LIQ	NA/IS	7.85	369
Lead	ND	ND	ND/ND	ND	ND	1.14	NA/LIQ	NA/IS	39.8	ND
Metals, Total										
Silver	91	NR	ND	NR	ND	NR	ND	NR	174	NR
Barium	105	NR	198	NR	869	NR	ND	NR	61.8	NR
Cadmium	2990	NR	4.5	NR	2190	NR	3.9	NR	213	NR
Chromium	57600	NR	245	NR	66500	NR	ND	NR	212	NR
Lead	182	NR	23.1	NR	19300	NR	24	NR	316	NR

NOTES: J = Indicates an estimated value. This flag is used when the concentration in the sample is outside the instrument calibration range or the identity of the compound is tentative.

ND = Not Detected

NR = Analysis for this parameter was not requested.

NA/IS = Not Analyzed. Insufficient sample was available for analysis.

NA/LIQ = Liquid samples are not extracted. EP Toxicity concentrations are measured by analysis of the liquid, as is, for total metals.



- The bilge emptying/cleaning sludge waste sample (WS-4) separated into aqueous and oil phases during analysis, both of which were analyzed. Although metals were not detectable in the water phase, chromium leached from the oil phase. However, the concentrations of chromium were well below the EP Toxicity characteristic limit.
- The painting operations waste sample (WS-6) exceeded the EP Toxicity characteristic limit of 1 mg/L for cadmium indicating that if not otherwise listed, it would be a HW due to EP Toxicity.
- The fluids changeout waste sample (WS-11) contained insufficient solids to perform the extraction procedure. For liquid waste, the total metals analysis is used as the measure of EP Toxicity. Based on total metals analysis, this waste exceeds the EP toxicity limits of 5 mg/kg for lead and 1 mg/kg for cadmium.
- The cleaning solvents waste sample (WS-13) exceeded the EP Toxicity limits for cadmium, chromium, and lead of 1, 5, and 5 mg/L, respectively.

### 3.2.3 Results of Ash Characterization

Table 3-3 presented the results of analyses of waste and ash samples for organic compounds (pesticide/PCBs, volatile organic compounds, semivolatile organic compounds). Results are not reported for the fluids changeout waste ash (WS-11A) because, as shown in Table 3-2, this waste contains only 0.87 percent ash and sufficient ash could not be generated for laboratory analysis. Comparison of the concentrations of these compounds present in the wastes and the corresponding concentrations present in the ashes indicates that the majority of organic compounds present in the waste samples are not present in the corresponding ash samples even though the ash tests are conducted well below typical incineration temperatures. This confirms that nearly complete destruction of organic compounds should be achievable by thermal treatment.

Table 3-4 presented the results of analysis of waste and ash samples for inorganic compounds. Inspection of the EP Leachate results for the ash indicates the following:

- The IWTP sludge waste ash sample (WS-1A) exceeded the EP Toxicity characteristic limit of 5 ppm for chromium. The waste sample (WS-1) originally passed the EP Toxicity characteristic, but it contained a high concentration of total metals. This is because the solubility of metal hydroxides in water is very low at the high pH associated with lime sludge. Upon

incinerating this waste, metal hydroxides will be converted into more leachable forms as discussed in Subsection 3.1. The concentrations of chromium in the ash are also greater than the BDAT treatment standards for this waste. Consequently, this ash could not be disposed of at a HW landfill without further treatment.

- EP leachate from the bilge emptying/cleaning sludge waste ash sample (WS-4A) contained only cadmium, and the level was below the EP Toxicity characteristic limit. The total metals concentrations for this waste sample indicate that it has a relatively low total RCRA metals content.
- The painting operations waste ash sample (WS-6A) exceeded the EP Toxicity characteristic limit of 1 mg/L for cadmium. The higher concentration of cadmium found in the leachate from the ash relative to the waste is likely due to the concentrative effect of incinerating wastes containing metals.
- A sufficient sample of ash for analysis could not be generated from the fluids changeout waste (WS-11) because this waste contains less than 1 percent ash by weight. Although the EP leachate analysis could not be performed, the total metals analysis of the waste sample (WS-11) indicates that the waste contains cadmium and lead. This waste is similar to the bilge emptying sludge sample (WS-4), in that both are oily wastes and contained similar concentrations of cadmium and lead. However, the ash constituents and EP Toxicity leachate metals concentrations may differ, particularly since the metals in the fluids changeout waste will be concentrated in a smaller quantity of ash. Thus, it is difficult to predict if this waste would exceed the EP Toxicity characteristic limits.
- The cleaning solvents waste ash sample (WS-13A) exceeded the EP Toxicity characteristic limit of 5 ppm for chromium.

The analytical results presented herein are based on analysis of wastes from two Navy facilities and may not be representative of the waste streams throughout the Navy. Although ash generated from laboratory incineration of waste will not be identical to the ash produced by a full-scale incinerator, and the ash samples may not be representative of these wastes Navy-wide, the following conclusions can be made based on an evaluation of the analytical results:

- The ashes produced from incineration of Navy wastes will require disposal as a HW due to the EP Toxicity of the ashes. Should the Navy intend to reduce future liabilities associated with land disposal of HW residues, ash treatment will be required to delist the waste.
- The IWTP sludge (WS-1) tested (or sludge from similar IWTP processes) should not be incinerated. The raw waste appears<sup>1</sup> to meet BDAT treatment standards for land disposal. However, after incineration the ash from this waste exceeds the BDAT treatment standards and would require additional treatment. The concentrations of organics in the waste should not preclude land disposal provided the IWTP sludge is not also considered an F001-F005 waste due to mixing with waste solvents.
- Provided subsequent analyses do not indicate that the IWTP sludge (WS-1) leaches nickel, the Navy should consider delisting Norfolk NAD IWTP sludge because it did not leach any EP toxic metals. The Navy should also consider analysis of IWTP sludge from other facilities to determine if their sludges can be delisted on a case-by-case basis.

Table 3-5 presents an estimate of the reduction in waste quantity that may be expected from incinerating the wastes identified as potential candidates for incineration. Incineration of the wastes identified as clearly incineratable results in an approximately 95 percent reduction in the quantity of waste, while the quantity of waste reduction associated with those wastes identified as potentially incineratable is only about 77 percent due to the presence of inorganics in these wastes. It should be noted that the ash contents used to calculate the waste quantity reduction are either estimated or based on analysis of samples of those process wastes from one Navy facility. Since these samples may not be representative of these process wastes at other Navy facilities, the quantity of waste reduction is approximate.

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<sup>1</sup>The sample achieved the F006 BDAT treatment standards for cadmium, chromium, lead, and silver. It is not certain if the sample achieved the standard for nickel because analysis for this compound was not part of the analytical program.

Table 3-5

Waste Reduction Resulting from  
Incineration of Navy Hazardous Wastes

Waste ID	Waste and Process	Quantity Generated <sup>a</sup> (tons)	Per- cent Ash	Ash Remaining After Incineration (tons)
CLEARLY INCINERATABLE				
3	Spent carbon from ordnance operations	33 <sup>b</sup>	5 <sup>b</sup>	2
4	Sludges from bilge emptying/cleaning	312	6.5	20
6	Waste solvents/residues from painting operations	530	12.4	66
7	Waste explosives/propellants from munitions demilitarization	3,649	2 <sup>b</sup>	73
11	Oils/sludges from fluids changeout	2,681	0.8	21
13	Cleaning solvents	530	33.9	180
17	Solvents/residues from chemical paint stripping	<u>904</u>	12 <sup>b</sup>	<u>108</u>
	SUBTOTAL	8,639	--	470
POTENTIALLY INCINERATABLE				
1	Sludge from IWTP	7,142	39.1	2,792
5	Residues from abrasive blasting	<u>6,662</u>	30 <sup>b</sup>	<u>1,999</u>
	SUBTOTAL	<u>13,804</u>	--	<u>4,791</u>
	TOTAL	22,443	--	5,261

<sup>a</sup>Calendar year 1985.

<sup>b</sup>Estimated.

The following subsection discusses some of the regulatory requirements for ash disposal based on the analytical results presented in this subsection.

### 3 3 REGULATORY REQUIREMENTS

The ash generated from the incineration of HW is considered a HW by virtue of RCRA's "derived from" rule [31]. This rule states that any residue resulting from the treatment of a HW, including ash, is a HW and must be managed as such. Treatment residues, such as ash, that are disposed of at HW landfills are subject to the additional requirements of the RCRA land ban. The land ban requires that the treatment residue resulting from certain HWs must meet the BDAT treatment standards in order to be disposed of at a HW landfill. When two or more wastes that are subject to the land ban are mixed, the most stringent BDAT standards apply [32].

Results of analyses of the ashes generated from samples of Navy HWs that were presented in Subsection 3.2.3 indicate that the IWTP sludge ash sample (WS-1) exceed the BDAT treatment standards for land disposal of this waste while the raw waste did not. Additional treatment of this ash would be required before the ash could be disposed of in a HW landfill. As discussed above, if this waste sample is characteristic of all IWTP sludge, it should not be incinerated prior to disposal.

BDAT standards for heavy metals have not been established for the other wastes tested; therefore, they could be disposed of in a HW landfill without further treatment. Should these other wastes be incinerated with the IWTP sludge, the combined ash would be subject to the treatment standards for IWTP sludge by virtue of RCRA's "mixture rule."

The presence of heavy metals in these ash samples would prevent the disposal of the ash as a nonhazardous waste without further treatment. Since disposal costs for nonhazardous wastes are substantially less than disposal costs for HWs, the disposal of ash as nonhazardous wastes is financially attractive. Ash treatment may also be desirable to achieve complete detoxification of Navy wastes and reduce future liabilities associated with land disposal of HW residues.

In order to dispose of the ash residue from incineration of Navy HWs as a nonhazardous waste, a "delisting" petition must be submitted to the U.S. EPA [33]. The petition must demonstrate that the residual(s) resulting from the treatment of a HW are no longer hazardous because of one of the following reasons:

- The waste does not contain significant concentrations of the constituents for which it was originally listed.
- The waste contains the constituents for which it was originally listed at relatively low concentrations or in an immobile form.
- The waste does not contain significant levels of hazardous constituents other than those for which the waste is listed.

In order to delist ash generated from the incineration of Navy HWs, additional treatment of the ash to remove or immobilize the heavy metals would be required. Section 4 of this report presents technologies that might be applicable to treatment of Navy ash.

## SECTION 4

### ASH TREATMENT TECHNOLOGIES

Ash from the incineration of listed hazardous wastes (HWs) must be managed as a HW under U.S. EPA HW regulations unless it is demonstrated that the constituents of the ash are nonhazardous and a delisting petition is submitted to and approved by the U.S. EPA or states authorized to administer the RCRA program. In the delisting petition, the generator must demonstrate that the listed waste is not hazardous because of one of the following reasons:

- The waste does not exhibit the characteristics or contain the constituents for which it was originally listed.
- The waste contains the constituents for which it was originally listed at relatively low concentrations or in an immobile form.
- The waste does not contain constituents other than those for which the waste is listed.

The constituents of Navy wastes that make them HWs include organic and inorganic compounds. The organic compounds of these wastes would be almost completely destroyed during incineration and would be expected to be found at relatively low concentrations in the ash. The inorganic compounds are not destroyed during incineration and would be concentrated in the ash. Although the concentrations of organic compounds in the ash would be relatively low, the presence of high concentrations of inorganic compounds in the ash would prevent ash from being delisted as a HW. Analytical results for ash samples of several Navy waste streams presented in Section 3 indicate that the ash could not be delisted without further treatment. Removal or immobilization of the hazardous inorganic constituents of the ash would make it possible to delist the ash and dispose of it as a nonhazardous waste reducing both disposal cost and future liability.

This section of the report identifies technologies with potential for removing or immobilizing the hazardous constituents in the ash so that it may be disposed of as a nonhazardous waste. Each technology is described and evaluated on the basis of performance and implementation criteria and recommendations are made for laboratory testing and evaluation.

#### 4.1 IDENTIFICATION OF ASH TREATMENT TECHNOLOGIES

Technologies capable of removing or immobilizing the hazardous inorganic constituents of incinerator ashes were identified through a literature search of the following computerized scientific and engineering databases:

- National Technical Information Service (NTIS).
- Compendex Plus (Engineering Index).
- Enviroline.
- Pollution Abstracts.
- Environmental Bibliography.
- Water Resource Abstracts.
- Current Technology Index.
- Japan Technology.

This search identified several technologies that have been evaluated for treating municipal solid waste incinerator and municipal sewage sludge incinerator ashes. These technologies are relevant because municipal solid waste and sewage sludge incinerator ashes may have chemical and physical properties similar to HW incinerator ashes.

Additional ash treatment technologies identified can be categorized as standard hydrometallurgical and HW treatment technologies for treating inorganic wastes.

The technologies that were identified are summarized in Table 4-1. These technologies may be categorized by type of process and approach to metals treatment into the following categories:

- Stabilization and fixation technologies that involve incorporating the ash in a cementitious or polymeric matrix and may also involve the precipitation of metals within this matrix as metal hydroxides, silicates, or other insoluble forms.
- Extraction or metal recovery technologies that use an acid solution to extract the metals from the ash to render the ash nonhazardous. The metals contained in extract solution are subsequently recovered in purified form for reuse or resale.



Table 4-1

## Potential Ash Treatment Technologies

Technological Category and Process	Process Type		Treatment Type		
	Sequential	Post-Incin	Phys	Chem	P/C
Extraction					
Ferrite		X		X	
Chemical precipitation		X		X	
Ion exchange		X		X	
Electrodeposition		X		X	
Stabilization/Fixation					
Cement pozzolans		X			X
Ash amendment		X			X
Microencapsulation		X	X		
Thermal					
Molten glass	X	X			X
Roasting	X	X			X
Slagging kiln	X				X

## Notes:

## Process Types:

Sequential - Process treats waste and ash concurrently in the thermal treatment unit so that a post-incineration ash treatment step is unnecessary.

Post-incineration - Process treats ash following incineration.

## Treatment Types:

Phys - Physical changes in the ash reduce the availability of the hazardous constituents in the ash.

Chem - Chemical changes in the ash reduce the availability of the hazardous constituents in the ash.

P/C - Physical and/or chemical changes in the ash reduce the availability of the hazardous constituents in the ash.

- Thermal technologies that treat metals by either incorporating the ash in a glass-like matrix (high temperature stabilization technologies), reducing the solubility of the metals by reacting to a form less soluble compounds, or chemically binding with the metals.

The subsections that follow describe each of the ash treatment technologies presented in Table 4-1 including the following information for each technology:

- Theory or approach to metals treatment.
- Process descriptions and block diagrams of process steps.
- Developmental status.
- Treatment effectiveness.
- Residuals generated and their treatment/disposal.
- Potential disqualifiers.

#### 4.2 STABILIZATION/FIXATION TECHNOLOGIES

Stabilization/fixation technologies render the ash nonhazardous by immobilizing the hazardous constituents by one or more of the following techniques:

- Changing the hazardous constituents into insoluble forms.
- Binding them in an immobile, insoluble matrix.
- Binding them in a matrix that minimizes the material surface exposed to leaching.

There are several commercial stabilization processes that have been used to treat industrial wastes and radioactive sludges. Some of the commercial processes are proprietary, but all essentially use one of two techniques for stabilization: cement/lime pozzolan admixture and microencapsulation. Both techniques involve mixing the waste with additives and allowing sufficient time for the product to cure.

The block diagram for a typical stabilization/fixation process is shown in Figure 4-1. Ash would be mixed with the additive(s) to produce a matrix that could be placed into molds or directly into landfills for disposal.

The following subsections describe several stabilization/fixation processes.

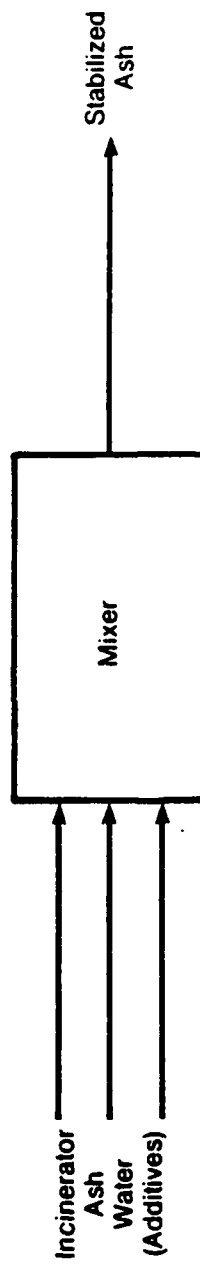


FIGURE 4-1 BLOCK DIAGRAM FOR STABILIZATION/FIXATION PROCESSES

#### 4.2.1 Cement and Lime Pozzolans

##### 4.2.1.1 Theory

Cement and lime pozzolan techniques involve the use of additives to form a concrete-type material. The primary additives in the cement pozzolan technique are Portland cement and water. The lime pozzolan techniques make use of the reaction of lime with silica and water to form a hard, concrete-like material, often called pozzolonic concrete. Additives like cement kiln dust and other (possibly proprietary) materials are added to the processes in order to increase the strength of the concrete or to retard the migration of metals in the concrete.

The cement/lime pozzolan processes alter two major chemical properties of the hazardous constituents of the waste: solubility and concentration. The solubility of the constituents is affected by alteration of the pH of the waste, chemical reaction to form a less soluble form of the constituent, or complexing or sequestering the contaminant in the matrix. Metals undergo a chemical reaction with the reagents to form nearly insoluble hydroxides or silicates. The concentrations of hazardous constituents are altered by dilution with the admixed material.

The presence of materials such as sulfates, chlorides, metallic anions such as arsenate and borates, and high concentrations of organic materials may interfere with solidification. However, these compounds are not expected to be present at high concentrations in Navy ash.

Figure 4-1 presents a block flow diagram for ash stabilization. Ash would be combined with the cement/lime additive and water in a screw mixer. Ash to additive ratios depend on the chemical properties of the ash and additive, but could range from 1:1 to 1:2. The cement-like product could be molded into blocks, briquettes, or pellets and subsequently landfilled.

##### 4.2.1.2 Developmental Status

The cement/lime pozzolan processes are commercially available from a variety of sources. Significant operating experience exists for use of this technology with both organic and inorganic waste streams. The U.S. EPA has selected this technology as the Best Demonstrated Applicable Technology (BDAT) for the treatment of ashes from the incineration of certain heavy metal containing wastes [34].

#### 4.2.1.3 Effectiveness

The technology can be very effective in immobilizing metals in certain waste streams including ashes from the incineration of heavy metal containing wastes [34]. As noted above, the U.S. EPA has selected this technology as the BDAT for the treatment of certain heavy metal containing wastes and ashes. Table 4-2 presents a comparison of metal plating waste characteristics before and after stabilization for several commercial stabilization agents and shows the EP Toxicity characteristic levels required for land disposal.

#### 4.2.1.4 Residuals Treatment/Disposal

The process generates no residual streams other than the stabilized product stream. Disposal requirements will depend on performance relative to EP Toxicity, BDAT, and delisting criteria.

#### 4.2.1.5 Potential Disqualifiers

Potential disqualifiers of cement and lime pozzolans include:

- Under severe, strongly acidic conditions the material can destabilize, but these conditions are not expected in the environment in the short term. The long-term stability of cement/lime pozzolans has not been demonstrated.
- The volume and weight of the waste are increased due to the addition of stabilizing agents and water. This disadvantage is offset if the waste can be delisted and disposed of as a nonhazardous waste because disposal costs for nonhazardous wastes are significantly less than disposal costs for HWs.

#### 4.2.2 Ash Amendment with Lime, Ammonium Phosphate, or Potassium Phosphate

##### 4.2.2.1 Theory

This technology is similar to the cement/lime pozzolan technology in that reagents are added to the residue, and they react with the metals to form nearly insoluble compounds. However, where cement/lime pozzolan technologies use lime and silicates as reagents to form metal hydroxides and silicates, this technology uses lime and ammonium or potassium phosphates to form metals oxides or phosphates.

Table 4-2

Comparison of Raw Waste EP Toxicity Before and After  
Stabilization for Several Wastes and Stabilization Processes

Compound	EP Toxicity Characteristic (mg/L)	EP Leachate	
		Before Treatment (mg/L)	After Treatment (mg/L)
Sample 1 <sup>a</sup>			
Cd	1	782	2.7
Cr	5	3,890	0.18
Cu	NE	25,500	0.36
Ni	NE	5,800	1.15
Pb	5	2,000	0.017
Zn	NE	28,700	25
Sample 2 <sup>a</sup>			
Cd	1	910	2.3
Cr	5	535	0.10
Cu	NE	1,850	0.64
Ni	NE	5,800	0.95
Pb	5	0.74	0.013
Zn	NE	5,400	5.0
Sample 3 <sup>b</sup>			
Cd	1	1	0.10
Cr	5	214	0.100
Cu	NE	NR	NR
Ni	NE	NR	NR
Pb	5	216	0.120
Zn	NE	NR	NR

## Notes:

<sup>a</sup>Source: [35].<sup>b</sup>Source: [36].

NE = None established.

NR = Not reported.

Figure 4-1 presents a block flow diagram for ash amendment. Ash would be combined with the additive(s) and water, if necessary, in a screw mixer. Ash to additive ratios depend on the chemical properties of the ash and additive, but could range from 1:1 to 1:2.

#### 4.2.2.2 Developmental Status

Bench-scale tests of this process have been conducted with municipal solid waste incinerator ash. Due to the simplicity of the process and its similarity to cement and lime pozzolanic stabilization, scaleup should be relatively straightforward. The process has not been applied to HW incinerator ash, however.

#### 4.2.2.3 Effectiveness

Bench-scale tests indicate that municipal solid waste incinerator ash that would fail the EP Toxicity test without treatment can pass the EP Toxicity test after treatment [37]. However, the process has not been applied to HW incinerator ash. The process may not be effective in treating the expected high metal content of Navy ash.

#### 4.2.2.4 Residuals Treatment/Disposal

The process does not generate residual streams other than the stabilized product stream. Disposal requirements will depend on performance relative to EP Toxicity, BDAT, and delisting criteria.

#### 4.2.2.5 Potential Disqualifiers

Potential disqualifiers for ash amendment include the following:

- Ash amendment has not been proven for HW stabilization; it may not be effective for higher metals concentrations.
- Under severe, highly acidic conditions the material can destabilize, but these conditions are not expected in the environment.
- The volume and weight of the waste are increased due to the addition of stabilizing agents and water. This disadvantage is offset if the waste can be delisted and disposed of as a nonhazardous waste because disposal costs for nonhazardous wastes are significantly less than disposal costs for HWs.
- Reagent costs appear to be higher than cement/lime pozzolans.

- The long-term stability of the amended ash has not been demonstrated.

#### 4.2.3 Microencapsulation

##### 4.2.3.1 Theory

In this process, contaminant particles in solid or liquid waste are immobilized by encapsulation materials that create small-scale encapsulation cells. The encapsulation technologies include polymers like polyethylene and other thermoplastics such as asphalt bitumen.

Figure 4-2 presents a block flow diagram of the microencapsulation process. Ash would be mixed with the polymeric substance in an extruder to form a product in which the contaminants are encased in a polymer matrix that is dispersed throughout the ash.

The SEALOSAFE process is a commercial, full-scale method used to treat wastes. This process is operated under the trade name of STABLEX. The process consists of thorough mixing with a monomer and polymerization to form a slurry that hardens over 3 days to form a rock-like material. The permeability of the product is less than that of clays or concrete. The encapsulation materials are proprietary and have not been described.

Asphalt and asphalt/sulfur blends have also been used to encapsulate metals and form the basis of another full-scale process called the Volume Reduction and Solidification System (VRS). The VRS process uses an extruder that simultaneously evaporates water from the waste while mixing it into the asphalt binder. The homogenized waste/asphalt mix is then discharged into containers where the mixture cools down. Volume reductions of 2.5 to 5 have been reported for granular wastes after cooling of the waste/asphalt mix [38].

Another process involves the use of an organic polymer modified gypsum cement called Envirostone Cement, manufactured by U.S. Gypsum Company. This process is a hybrid variation of cement stabilization processes combining both inorganic cement with organic binders [39].

##### 4.2.3.2 Developmental Status

Both the SEALOSAFE and VRS processes are commercial, full-scale treatment technologies.



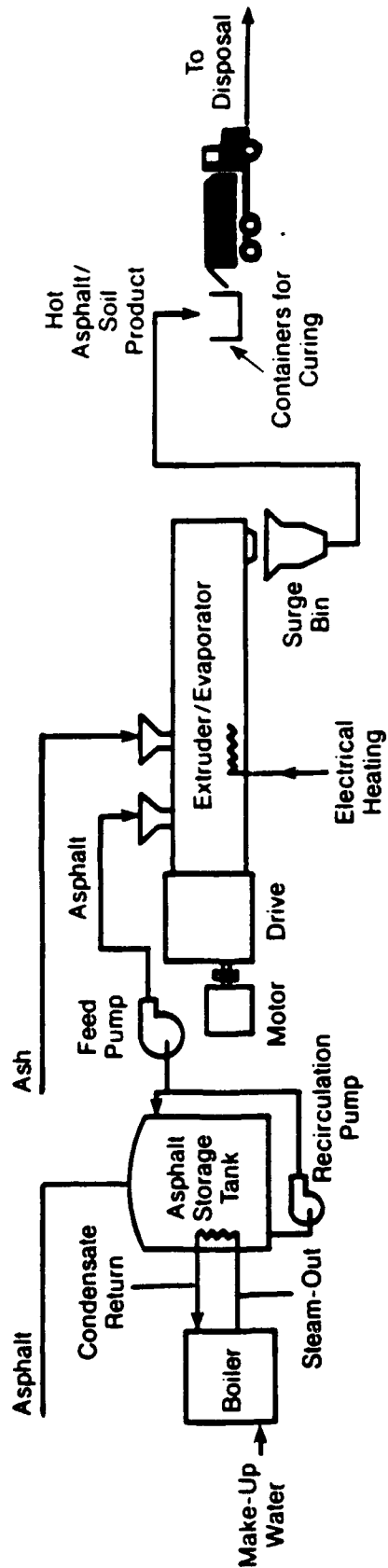


FIGURE 4-2 FLOW DIAGRAM WITH MAJOR EQUIPMENT FOR  
ASH MICROENCAPSULATION

#### 4.2.3.3 Effectiveness

Leachability and mechanical tests performed on both the STABLEX product and the asphalt/sulfur blend show that they offer strong resistance to chemical attack and withstand mechanical stresses. Metals are effectively immobilized in the additive matrix, which is dispersed throughout the waste.

Chappell and Willetts [40] have reviewed independent test data on waste treated by the STABLEX process to verify the manufacturer's claim that the process effectively isolates heavy metals. Leachability tests similar to the TCLP indicate that the leachate contained very low concentrations (<1 ppm total) of metal.

Brenner and Rugg [38] have investigated the effectiveness of using asphalt and asphalt/sulfur blends to encapsulate metals. In their experiments molten sulfur and liquefied asphalt were blended for 8 minutes to form an emulsion at a temperature between 285 and 300°F. This emulsion was then immediately mixed for 2 minutes with a preheated "simulated waste" like copper sulfate, at a temperature between 290 and 305°F. Their results showed that the best results, in terms of binding, were achieved using a ratio of 60 percent waste and 40 percent asphalt/sulfur binder. The product exhibited strong resistance to chemical and mechanical stresses. Minor problems with increased leachate due to partially encapsulated particles were solved by applying a thin exterior coating of asphalt by hot spray or dipping [38].

The Envirostone process has been applied to radioactive wastes. Leaching tests indicate low diffusivities of radioactive isotopes from the treated waste [41]. The developer states that some formulation changes have been necessary for chemical waste treatment [42]. Data on the leachability of chemical wastes from the Envirostone product have not been presented.

#### 4.2.3.4 Residuals Treatment/Disposal

The process does not generate residual streams other than the microencapsulated product stream, which offers strong resistance to leaching and withstands mechanical stresses.

#### 4.2.3.5 Potential Disqualifiers

Potential disqualifiers include:

- Operating costs for microencapsulation are expected to be higher than stabilization due to reagent costs and energy requirements.

- The weight of the waste is increased due to the addition of the asphalt/sulfur blend. This disadvantage is offset if the waste can be delisted and disposed of as a nonhazardous waste because disposal costs for nonhazardous wastes are significantly less than disposal costs for HWs.
- The inorganic binders in the Envirostone product may destabilize under severe, strongly acidic conditions, but these conditions are not expected in the environment.

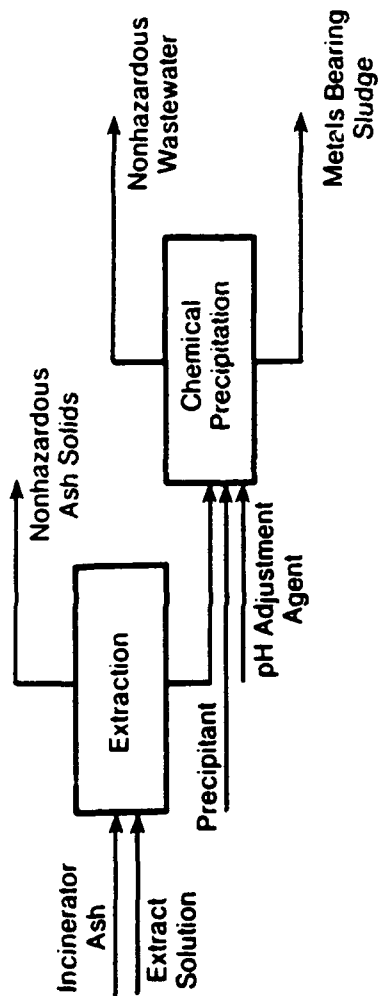
#### 4.3 EXTRACTION TECHNOLOGIES

Extraction technologies render the ash nonhazardous by removing the hazardous constituents from the ash using chelating agents or acidic or basic solutions. Other soluble nonhazardous ash constituents such as calcium, which is present at high concentrations in Navy IWT sludge, may also be removed from the ash, however. Downstream processing steps such as precipitation or metal recovery remove the hazardous metals from the extract solution. The presence of other soluble nonhazardous ash constituents such as calcium may complicate some of these downstream processing steps.

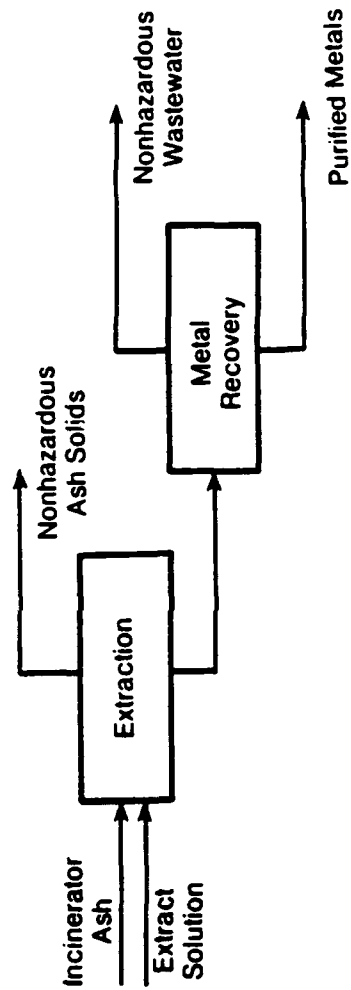
Figure 4-3a presents a block in diagram of the extraction step common to all extraction technologies. Two streams leave the extraction step of the process: insoluble ash solids and an extract solution containing solubilized metals.

Canadian researchers [43] have investigated the extraction of metals from sewage sludge incinerator ashes using a variety of solvents and solutions including water, acids and bases, ethylenediaminetetraacetic acid (EDTA), detergents, hydrogen peroxide, and sodium persulfate. The solvents had different extraction efficiencies for specific metals. One study [44] reported greatest overall toxic metals extraction with 60 percent sulfuric acid.

The insoluble ash solids leaving the extraction step should contain concentrations of metals and organics that make the solids acceptable for disposal as a nonhazardous waste. Oliver and Carey [44] report extraction of 5 to 100 percent of various metals present in incinerated sewage sludge ash. Table 4-3 presents their results obtained using hot 60 percent sulfuric acid. Extraction temperature, time, and ash to acid loading was not reported. The leachability of the ash before and after extraction was not determined.



(a) Chemical Precipitation



(b) Metal Recovery

FIGURE 4-3 BLOCK DIAGRAM OF GENERIC EXTRACTION TECHNOLOGIES INVOLVING (A) CHEMICAL PRECIPITATION, (B) METAL RECOVERY

Table 4-3

Effectiveness of Acid Extraction in Removing Individual  
Toxic Metals from Sewage Sludge Incinerator Ash

Element	Metals Concentration in Sewage Sludge Ash (mg/kg)*		Percent Extraction with 60% H <sub>2</sub> SO <sub>4</sub>	
	Range	Mean	Range	Mean
Cd	10-50	30	20-79	38
Cu	600-3,000	2,100	62-94	80
Fe	43,000-146,000	108,000	24-93	64
Pb	200-3,600	2,300	5-12	7
Ni	300-800	600	47-80	67
Mn	1,000-18,000	12,000	69-100	87

Source: [44].

Notes: \*Calculated from weigh. percent analysis.

Table 4-4 presents the metals concentrations in leachate from municipal solid waste incinerator fly ash before and after a sulfuric acid extraction. The extraction was performed at a pH of 5 to 5.5. Extraction time, temperature, and ash to acid loading was not reported [45]. Following extraction the ash-acid mixture was filtered and the ash cake washed. Although the results are not directly comparable to EP Toxicity limits because of differences in the extraction procedure, the data indicate that a low leaching ash cake can be obtained.

The extract solution will contain metals concentrations such that additional treatment of this solution is required prior to discharge. The metals may be removed from the extract solution using two techniques: chemical precipitation or metal recovery.

Block diagrams of metal removal operations by chemical precipitation and metal recovery techniques are shown in Figure 4-3b and 4-3c, respectively.

Chemical precipitation involves the formation of insoluble or slightly soluble salts by adjusting the solution pH to a point where the constituents to be removed have their lowest solubilities. Most chemical precipitation technologies will generate a sludge that may itself be a HW because of its metal content and leaching characteristics. If the precipitate is hazardous, the only benefit of extraction/precipitation would be volume reduction.

Metal recovery technologies will recover the metals in purified form so that they can be reused in the generating processes or sold. Metal recovery technologies that may be applicable include ion exchange and electrodeposition.

The following subsections describe extraction processes that use chemical precipitation and metal recovery technologies.

#### 4.3.1 Ferrite Process

##### 4.3.1.1 Theory

The ferrite process achieves metals treatment by chemically binding the heavy metals (M) in an insoluble ferrite ( $M_xFe_{(3-x)}O_4$ ) sludge via a two-step chemical reaction. The first reaction involves reaction of the acid-solubilized divalent heavy metal ion ( $M^{++}$ ) with  $Fe^{++}$  and hydroxide ( $OH^-$ ) to produce a mixed metal hydroxide:

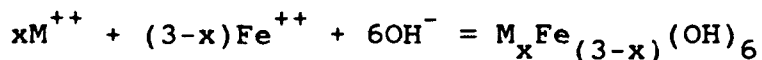


Table 4-4

Comparison of Metals Concentration in Municipal  
Solid Waste Incinerator Fly Ash Before and  
After Extraction

Element	Typical Metals Concentration in Untreated Fly Ash		EP Toxicity Characteristic Leachate (mg/L)	Typical Metals Concentrations in Acid Extracted Fly Ash Leachate <sup>a,b</sup> (mg/L)
	Total (mg/kg)	Leachate <sup>a</sup> (mg/L)		
T-Cr	146.6-150.2	0.473-0.491	5	<0.05
Cr <sub>6+</sub>	5.8-6.3	0.238-0.243	-	<0.05
As	25.5-91.7	<0.01-0.05	5	<0.05
Cd	324.6-418	3.90-26.7	1	<0.01
Pb	4,013-4,700	1.57-4.44	5	<0.1
Hg	2.4-10.54	0.0070-0.0104	0.2	<0.0005

Source: [45].

Notes:

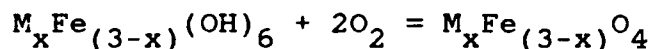
<sup>a</sup>Leachate is prepared as follows:

Ten grams of sample (water content <85 percent) is mixed in 100 mL water and the pH adjusted to between 5.8 and 6.3. The mixture is shaken continuously for 6 hours at a shaking amplitude of 40-50 mm and a frequency of 200 min<sup>-1</sup>. The mixture is filtered through glass fiber filter paper with a one micron pore diameter and the filtrate analyzed.

These data are not directly comparable to the EP Toxicity levels because the EP test involves a more vigorous extraction at a pH of 5.0 for 24 hours.

<sup>b</sup>Fly ash was treated by agitation with sulfuric acid at a pH between 5 and 5.5. The ash concentration in the extract solution was 25 percent. Extraction time and temperature were not reported. Insoluble ash solids were recovered by filtration, washed, and subjected to the leaching test. Metals concentrations in the supernatant and wash water were not reported.

The mixed metal hydroxide is subsequently oxidized to produce an insoluble metal ferrite ( $MFe_2O_4$ ) sludge. The literature [45] reports the unbalanced reaction



The fate of the six hydroxide ions in this reaction is not explained in the literature. It is hypothesized that the hydroxide ions will combine with excess cations present in the solution.

Because the heavy metal is chemically bound in the insoluble ferrite, it should have low EP Toxicity characteristics and, thus, it should be possible to dispose of the ferrite as a nonhazardous waste.

Figure 4-4 presents a block diagram of the process steps. The ash is mixed with a sulfuric acid solution that extracts the heavy metals from the ash. The acid and insoluble ash solids are separated by filtration. The insoluble ash solids are retained as filter cake. After cake washing to remove any residual acid and solubilized metals, the filter cake should contain concentrations of metals acceptable for disposal as a nonhazardous waste. The acid filtrate and cake washing water are combined and mixed with ferrous sulfate, which serves as the source of iron. The pH of this solution is then increased with sodium hydroxide. The final pH of this solution is not presented by the developers. It is then oxidized at 70°C for 1 to 2 hours by sparging air into the reactor. The oxidation product is the insoluble ferrite sludge that is kept in suspension in the reactor by thorough mixing. Upon completion of the reaction, the ferrite product is separated from the aqueous phase by filtration. Neither the pH nor the metals concentration of the supernatant are reported in the literature [45]. However, the supernatant is reportedly neutralized and discharged as a nonhazardous wastewater.

#### 4.3.1.2 Developmental Status

The Japanese may have full-scale treatment plants using the ferrite process for the treatment of heavy metal contaminated wastewater. They also have performed bench-top and pilot-plant testing of the process for treatment of electrostatic precipitator dusts. However, the ferrite process does not appear to have been commercialized for treating electrostatic precipitator dusts.

#### 4.3.1.3 Effectiveness

The data presented in Table 4-4 indicate that the insoluble ash solids that remain after acid extraction, filtration, and filter



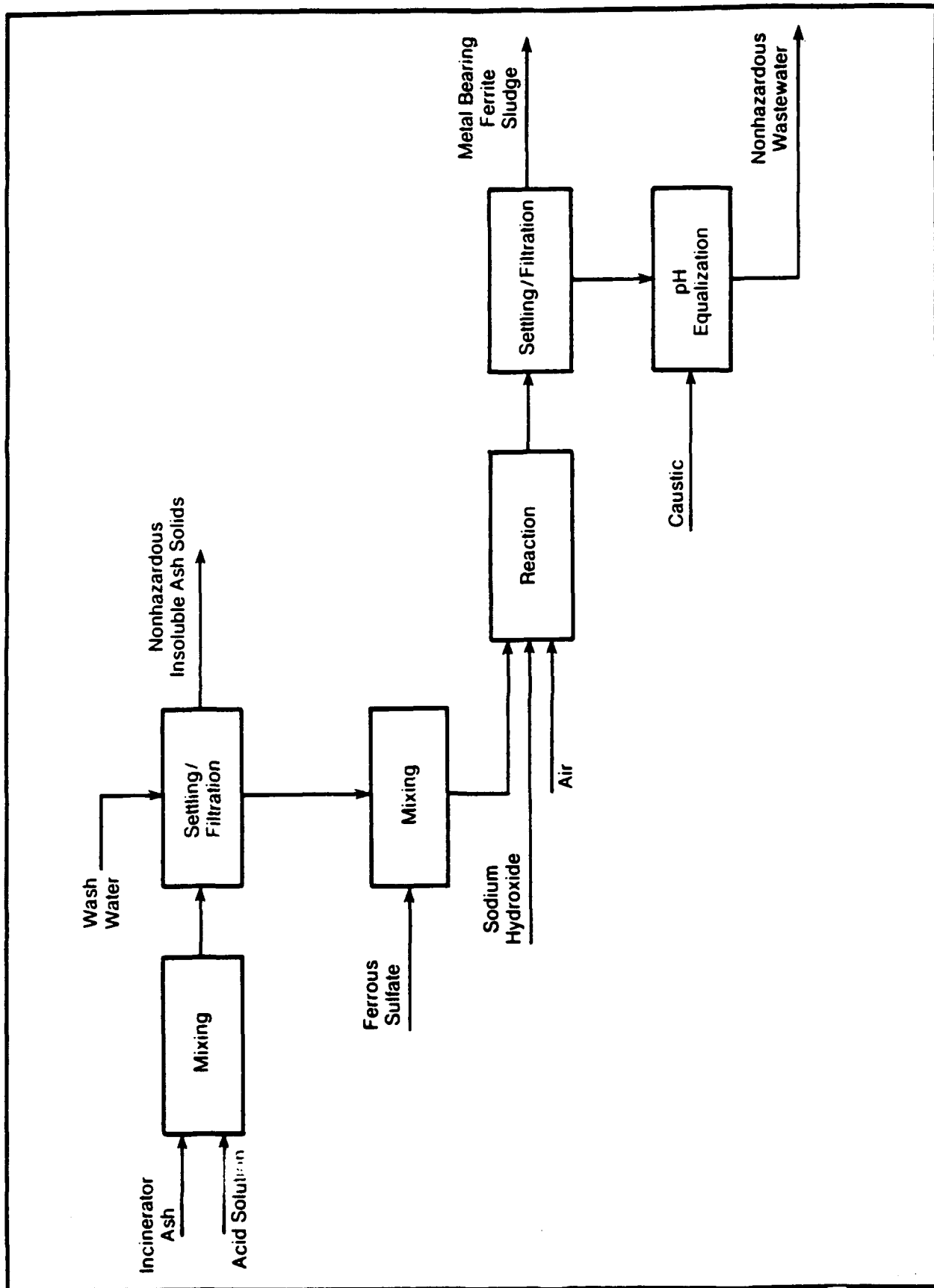


FIGURE 4-4 BLOCK DIAGRAM OF EXTRACTION/FERRITE REACTION PROCESS

cake washing contain concentrations of heavy metals that are acceptable under the EP Toxicity characteristic. These results were obtained from municipal solid waste incinerator fly ash. Similar results may not be obtained for Navy ash due to differences in the waste stream and the design and operation of municipal solid waste and HW incinerators. Data are not available on the leaching of the ferritized sludge; however, since the ferritized sludge is not a metal salt, the chemical bonds formed are covalent rather than ionic, and the supernatant pH is near the EP Toxicity test pH of 5.0, the divalent heavy metals bound in the ferritized sludge should not be leachable. Solubility data on the iron form of the metal ferritized sludge ( $\text{Fe}_3\text{O}_4$ ) indicate that this compound is insoluble in water [46]. Solubility data were not available for other metal ferrites.

It is not clear how trivalent heavy metals such as chromium are treated by this process, since the reactions involved in the process are for divalent heavy metals. It is hypothesized that trivalent metals would be coprecipitated in the ferrite sludge. Since trivalent metals may not be chemically bound as ferrite, they may be more readily leached from the ferrite sludge. Since chromium is expected to be the heavy metal present at greatest concentrations in Navy ash due to its use in electroplating operations, the ferrite process may not be effective in treating Navy ash.

The presence of other divalent metals such as calcium, which would be present from lime used in Navy industrial wastewater treatment processes, would increase the reagent requirements.

#### 4.3.1.4 Residuals Treatment/Disposal

The process generates a wastewater stream that requires neutralization prior to discharge. Heavy metals that are not completely reacted to form a ferrite product may coprecipitate with the ferrite sludge or remain in the wastewater stream requiring further treatment or disposal as HW.

#### 4.3.1.5 Potential Disqualifiers

Potential disqualifiers of the ferrite process include the following:

- Effectiveness for removing trivalent metals such as chromium from the extract are not known.
- Leaching data for the ferrite sludge are not available. Further processing and/or residuals disposal as HW will be necessary if the ferrite sludge exhibits unfavorable leaching characteristics.

- Capital costs of the ferrite process are expected to be higher than stabilization due to the number of processing steps and size of equipment required. Operating costs will be significant due to high reagent costs and the possibility that disposal as HW will be necessary.

#### 4.3.2 Chemical Precipitation

##### 4.3.2.1 Theory

Chemical precipitation removes dissolved metals from aqueous wastes by precipitating the metals from solution as hydroxides, sulfides, carbonates, or other insoluble salts. A solution containing the required precipitation reactant and acid or base is added to a solution to adjust the pH. This results in conversion to the insoluble salt at a pH where the constituents to be removed have their lowest solubility. For example, trivalent chromium could be precipitated as chromium hydroxide by the addition of calcium hydroxide according to the reaction:

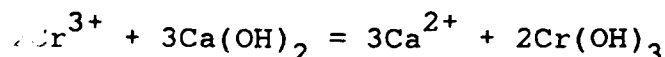


Figure 4-5 shows that chromium would precipitate as the hydroxide at a pH of about 8.5, and the concentration remaining in solution would be about 0.03 mg/L. This figure also shows that the mixtures of metals precipitate over the pH range of about 8.5 to 11.

Figure 4-6 presents a block diagram of a chemical precipitation process. The ash is mixed with sulfuric acid solution that extracts the heavy metals from the ash. The acid and insoluble ash solids are separated by settling and filtration. The insoluble ash solids are retained as filter cake that is washed to remove any residual acid and solubilized metals. The filter cake should contain concentrations of metals acceptable for disposal as a nonhazardous waste. The acid filtrate and cake washing water are combined and fed to the precipitator tank where chemical precipitants are added. Polymeric settling aids may also be added. The mixture is pumped to the clarifier where the precipitate settles out and is removed as a sludge. This sludge may be non-hazardous, but many such water treatment sludges are HWs due to their high heavy metal content. The effluent from the clarifier can be discharged to the sewer.

##### 4.3.2.2 Developmental Status

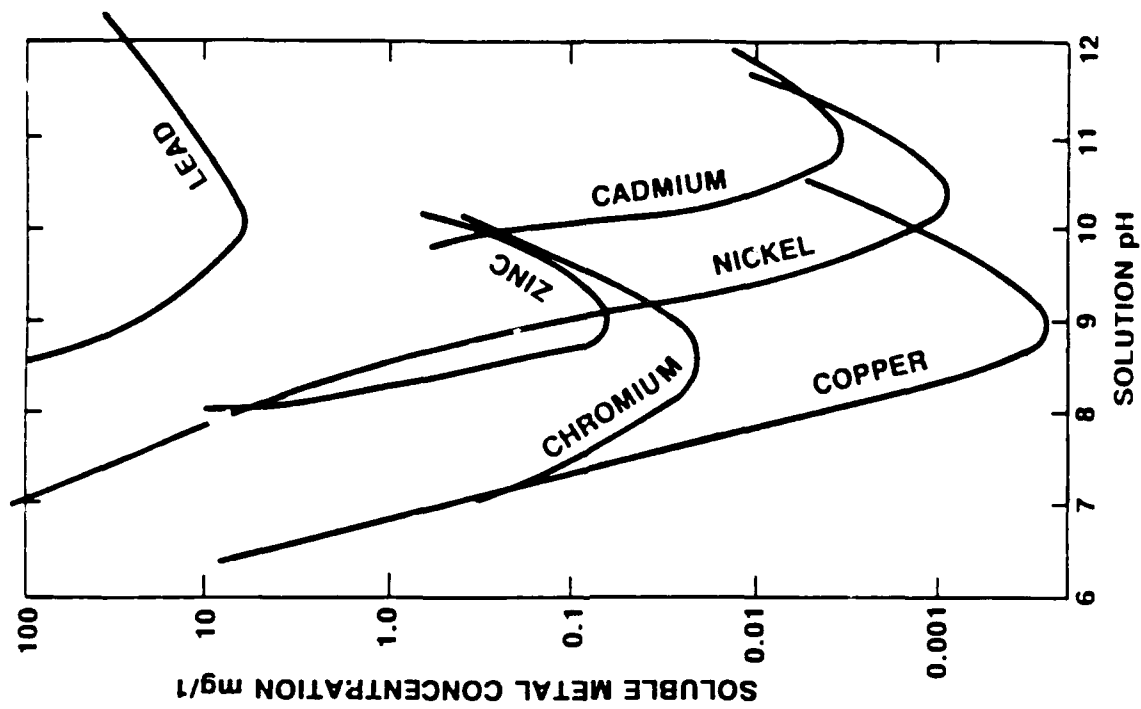
Chemical precipitation is a fully developed wastewater treatment technology. It is not known to have been used as an ash extract treatment technology.

# Precipitation Reactions

Divalent Metals (M = Cu, Ni, Zn, Cd, Pb):



Trivalent Metals (M = Cr):



Source: "A Compendium of Technologies Used in the Treatment of Hazardous Wastes," EPA/625/8-87/014, Sept. 1987

FIGURE 4-5 CHEMICAL PRECIPITATION OF HEAVY METALS FROM AQUEOUS SOLUTIONS

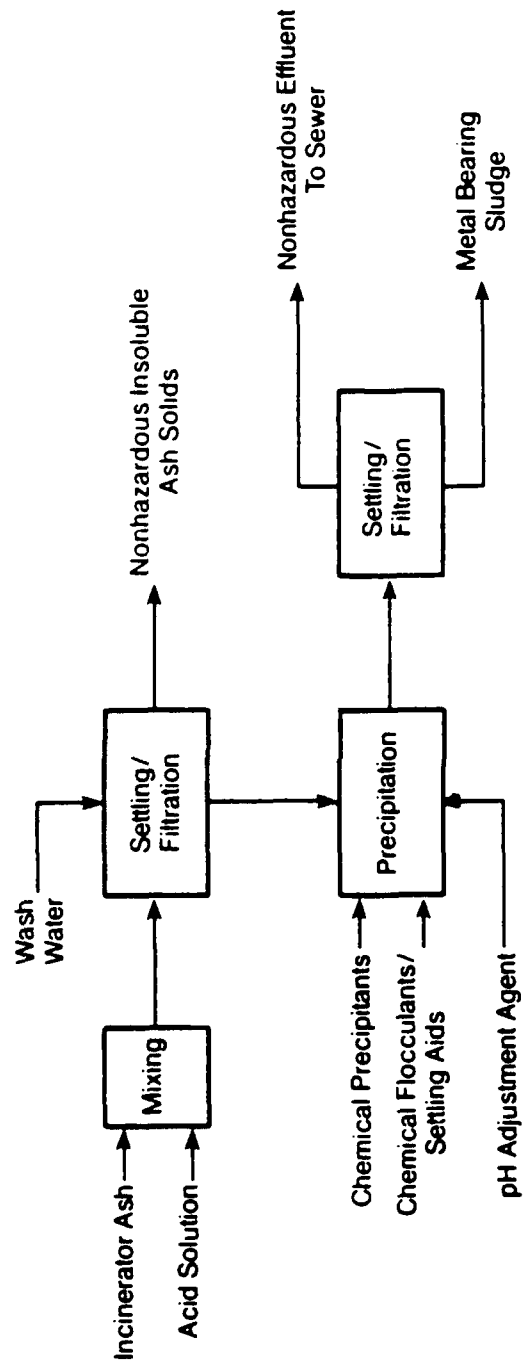


FIGURE 4-6 BLOCK DIAGRAM OF EXTRACTION/CHEMICAL PRECIPITATION PROCESS

#### 4.3.2.3 Effectiveness

The extraction step should be effective in removing heavy metals from the incinerator ash. However, once removed from the ash these metals must be removed from the extract solution. Chemical precipitation is effective in removing heavy metals from aqueous waste streams, but it generates a sludge that could potentially be a HW due to its heavy metal content. Since the volume of sludge generated may be significant relative to the original volume of incinerator ash and since the sludge may be hazardous, extraction followed by chemical precipitation is not considered to be an effective treatment for incinerator ash.

#### 4.3.2.4 Residual Treatment/Disposal

Two residual streams are produced by this process: a wastewater that may be discharged and a sludge that may be hazardous due to its metal content.

#### 4.3.2.5 Potential Disqualifiers

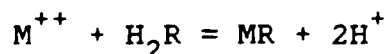
Potential disqualifiers for chemical precipitation include the following:

- Chemical precipitation generates waste sludge that may be hazardous and whose volume may be significant relative to the volume of the original ash. Leaching characteristics of the sludge are typically waste stream specific and would require testing.
- Capital costs of the process are expected to be higher than stabilization due to the number of processing steps and size of equipment required. Operating costs will be significant due to the use of chemical precipitants, reagents needed to increase the pH of the acidic extract to the pH required for precipitation, and sludge disposal.

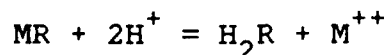
#### 4.3.3 Ion Exchange

##### 4.3.3.1 Theory

Ion exchange resins are specifically formulated resins having an "exchangeable" ion ( $H^+$ ) bound to the resin (R) with a "weak ionic" bond. In an ion exchange process for metals recovery, the toxic metal ion (M) in solution would be exchanged with a non-toxic ion ( $H^+$ ) and the metal bound to the resin according to the following reaction:



After all ion exchange sites are occupied by the metals, the ion exchange resin is said to be "spent." Spent resin is usually regenerated by exposing it to a very concentrated solution of the original exchange ion ( $H^+$ ), which reverses the ion selectivity preference and allows exchange to take place. This results in a regenerated resin and a concentrated solution of the metal ion according to the following reaction:



A solution of several metal species can be treated with ion exchange resin. However, the selectivity of any ion exchange resin for a given metal depends upon the properties of the resin and its functional exchange group, metal's concentration, the presence of other species, and pH.

Individual species of metals can be recovered by "selective elution" during the regeneration cycle. Selective elution involves regenerating the resin in steps with a different regenerant solution pH for each step.

Ion exchange resins that would be used in this application are of the strong or weak acid cation or chelating cation exchange type. These resins have a high affinity for heavy metal cations over alkali or alkaline earth metals such as sodium, potassium, calcium, and magnesium, which would also be present in the acid extract.

Since a resin's selectivity for specific metal ions differs, the resin must be selected to match the specific metals and concentrations present in the extract. Ions such as calcium or sodium, which may also be present in the extract, may compete for exchange sites and reduce the resin capacity.

Figure 4-7a presents a block diagram of an ion exchange process for the recovery of heavy metals from ash. The ash is mixed with a sulfuric acid solution that extracts the heavy metals from the ash. The acid and insoluble ash solids are separated by filtration. The insoluble ash solids are retained as filter cake that is washed to remove any residual acid and solubilized metals. The filter cake should be relatively free of leachable metals and acceptable for disposal as a nonhazardous waste. The acid filtrate and cake washing water are combined.

Depending on the resin used, pH adjustment may be required before the extract is passed through the ion exchanger. With weak acid or chelating cation resins, the pH of the extract would have to be increased to about 4 or 5 because these resins cannot tolerate more acidic conditions. Strong acid resins could tolerate an extract with a pH as low as 2. However, these resins

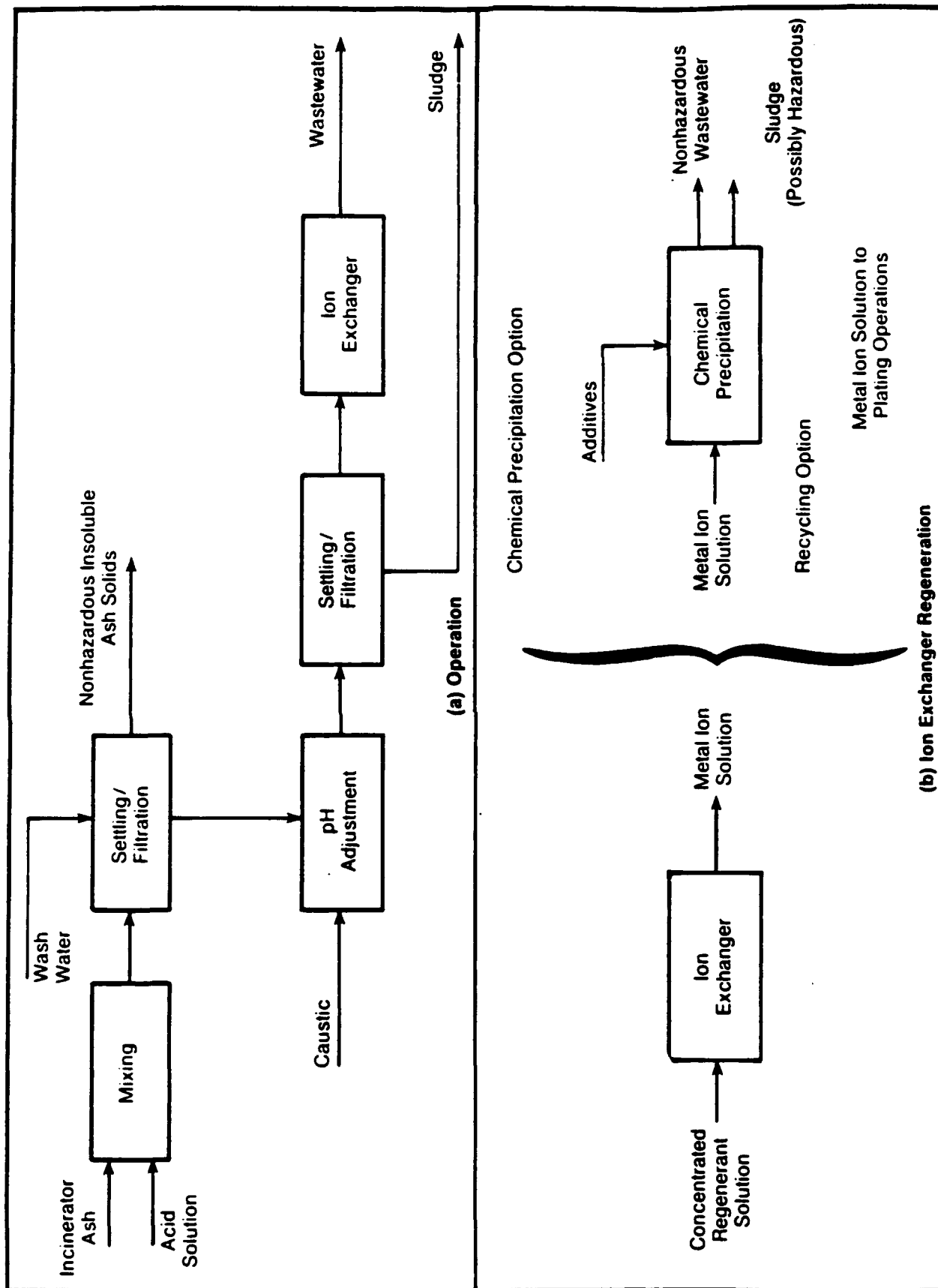


FIGURE 4-7 BLOCK DIAGRAM OF ION EXCHANGE PROCESS SHOWING (A) OPERATION AND, (B) REGENERATION



require larger volumes of acid regenerant, and the regenerant must be at a lower pH than weak acid or chelating resins.

Suspended solids content in the combined acid filtrate/cake washing solution should be less than 50 mg/L to prevent plugging of the resin beds.

Following pH adjustment, if necessary, the extract is passed through two ion exchange resin beds operated in series to remove the heavy metal ions from solution. The beds are operated in series for the following reasons:

- Metal loading rates are increased.
- Regenerant requirements are, therefore, reduced.
- The second column provides a backup to the first should the resin become exhausted prematurely.

The acid solution leaving the ion exchange beds may contain trace amounts of heavy metals. Some of the acid solution could be recycled and used as cake washing solution or neutralized and discharged. Neutralization of the acid solution may generate a sludge containing trace amounts of heavy metals that might require additional treatment to be disposed of as nonhazardous waste.

Figure 4-7b presents a block diagram of the resin regeneration cycle that is required when the resin becomes exhausted. The resin is regenerated and can be reused by pumping concentrated acid through the resin beds. Solutions containing mixtures of specific metal species can be recovered by regenerating the resin with different concentrations of regenerant. It may be possible to adapt the regenerant solution(s) for use in plating bath(s). If the regenerant cannot be used in plating baths, neutralization and chemical precipitation of the metals in the regenerant would be required. Chemical precipitation would produce a waste sludge that may be hazardous.

#### 4.3.3.2 Developmental Status

Ion exchange is a commercially available technology used for treatment of heavy metal contaminated wastewater streams in a variety of industries including metal plating and hydrometallurgy. Several manufacturers of ion exchange resins produce resins suitable for this application; however, this technology has not been identified with treatment of HW incinerator ash.

#### 4.3.3.3 Effectiveness

Ion exchange is a demonstrated technology for removing heavy metals from aqueous streams containing heavy metals such as hydrometallurgical leach solutions, plating baths, and plating operation rinse waters. The resin used must be selected carefully based on the types and concentrations of heavy metals present because of the selectivity of the resin for specific metal ions and competition between metal ions for resin exchange sites. Regenerant solutions will contain heavy metals that may be precipitated using chemical precipitation techniques or reused in plating solutions. Chemical precipitation techniques would generate a waste sludge that may be hazardous.

#### 4.3.3.4 Residuals Treatment/Disposal

Two residual streams are produced by this process: an acidic wastewater stream and a waste acid regenerant stream. The wastewater may require pH equalization prior to discharge. The waste acid regenerant will contain heavy metals that must be removed prior to discharge or reused in other processes such as electroplating operations. Heavy metals can be removed from the waste acid regenerant by chemical precipitation. Chemical precipitation will produce a waste sludge that may be hazardous.

#### 4.3.3.5 Potential Disqualifiers

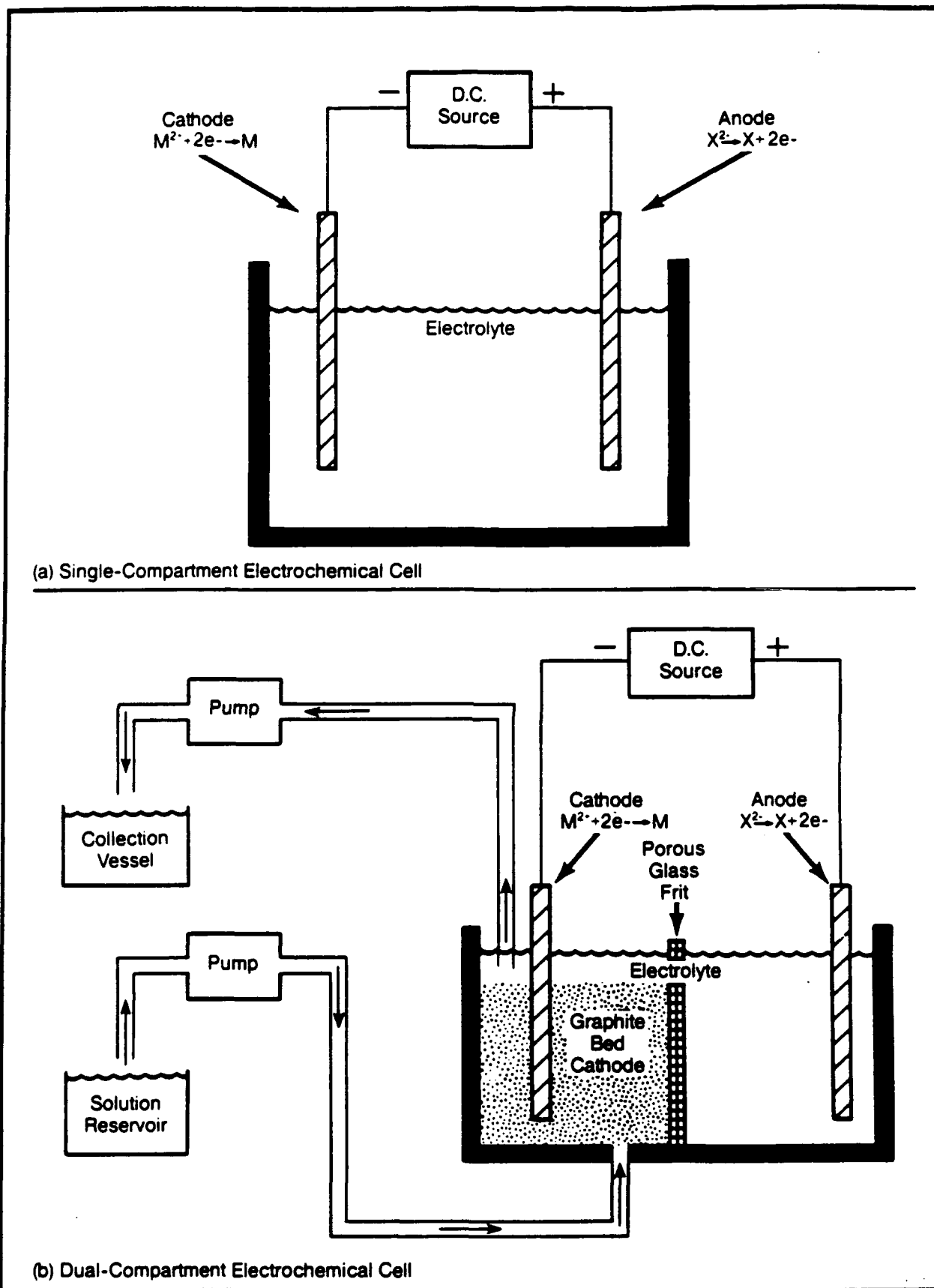
Potential disqualifiers of ion exchange include the following:

- The process may generate a hazardous sludge containing heavy metals if the regenerant cannot be reused in electroplating operations.
- Selectivity for and competition between specific cations may inhibit treatment.
- If levels of metals and competing ions in the extract solution are too high, the limited capacity of ion exchange resins will result in insufficient metals concentration in the extract to warrant using this technology.

#### 4.3.4 Electrodeposition

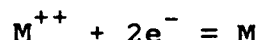
##### 4.3.4.1 Theory

A metal can be recovered from aqueous solutions of its salt by deposition onto an electrode in an electrolytic cell. A typical single-compartment electrolytic cell is shown in Figure 4-8a. It consists of two electrodes in the electrolyte solution containing metal ions. When a current is applied across the electrodes,



**FIGURE 4-8 SCHEMATICS OF SINGLE- AND DUAL-COMPARTMENT ELECTROCHEMICAL CELLS**

a reaction occurs at each electrode, such as the following general reduction reaction:



This results in the metal being deposited onto the negative electrode (cathode). The corresponding oxidation reaction that occurs at the anode is:

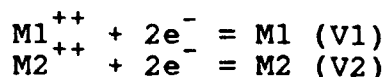


Similar reactions occur at the anode and cathode in the dual-compartment electrochemical cell shown in Figure 4-8b. This cell differs from the single compartment cell in the following respects:

- A porous, sintered glass frit separates the anode and cathode compartments.
- Granular graphite may be added to either electrode compartment to create a graphite bed electrode.
- The electrolyte can be continuously pumped through the cell. Electrolyte flow rates may be sufficiently great that the granular graphite bed is fluidized.

The advantage of the dual compartment cell is that fluidization of the graphite bed electrode enhances mass transfer, thereby increasing the plating efficiency.

A solution of several metal species may be treated by electro-deposition and purified metals recovered by selectively plating each species at a different voltage. For example, two different metal species, M1 and M2, contained in an electrolyte may be selectively recovered by plating M1 out of solution onto an electrode at voltage V1 and subsequently plating M2 onto a different electrode at a greater voltage V2 ( $V1 < V2$ ) as shown by the following reactions:



The efficiencies at which metals plate is a function of the electrolyte composition and mass transfer limitations near the electrodes. Interference by impurities is common.

A block diagram for the electrodeposition process for the recovery of heavy metals from ash is represented in Figure 4-3b. The ash is mixed with sulfuric acid solution that extracts the heavy metals from the ash. The acid and insoluble ash solids are separated by filtration. The insoluble ash solids are retained

as filter cake that is washed to remove any residual acid and solubilized metals. The filter cake should contain concentrations of metals acceptable for disposal as a nonhazardous waste. The acid filtrate and cake washing water are combined and fed to the electrolytic cell(s). The electrolytic cells may be operated in series at successively higher voltages so that the most easily reduced metals(s) plate out of solution in the initial cell(s). Eventually cell electrodes would build up metal deposits and require replacement. Spent electrodes with recovered metals deposited on them could be processed in house to recover metals, sent to a metal refiner for recovery, or disposed of as HW.

Canadian researchers [47] have studied the feasibility of metals recovery from municipal wastewater sludge incinerator ash using electrodeposition. Their studies used both single and dual-compartment, bench-scale electrochemical cells and indicated recovery of cadmium, copper, nickel, and zinc is best achieved with neutral 0.5 molar ammonium sulfate electrolyte. Optimum performance was obtained with fluidized bed graphite electrodes. However, metal concentrations remaining in the cell effluent are greater than U.S. EPA New Source Performance Standards (NSPS) effluent limitations that might be applicable (New Source Performance Standards for the Metal Finishing Point Source Category) [48]. Therefore, the cell effluent may require polishing such as chemical precipitation prior to discharge. Polishing of the cell effluent may generate a HW sludge.

#### 4.3.4.2 Developmental Status

Canadian researchers have studied the feasibility of recovering copper, zinc, nickel, and cadmium from municipal wastewater sludge incinerator ash in bench-scale experiments. The metals in the ash were solubilized using sulfuric acid. Due to the iron content of the ash, which complicated downstream processing steps, the sulfuric acid leachate was first neutralized with sodium hydroxide to precipitate the metals. Then, the heavy metals were resolubilized with a hot  $\text{NH}_4\text{OH}/(\text{NH}_4)_2\text{SO}_4$  mixture leaving iron in the solid phase. Electroplating removed between 90 to 99.9 percent of the copper, zinc, nickel, and cadmium from the ammonia solution.

#### 4.3.4.3 Effectiveness

As with other extraction technologies, the process may be effective in removing heavy metals from incinerator ash. However, once removed from the ash these metals must be removed from the extract solution. Electrodeposition can be effective in removing greater than 90 percent of the metals from the electrolyte; however, concentrations remaining in solution may still

be greater than applicable discharge criteria and require chemical precipitation to reduce metal concentrations to discharge criteria. The use of chemical precipitation as a polishing step may produce a HW sludge.

#### 4.3.4.4 Residuals Treatment/Disposal

The process generates two residual streams: spent electrolyte and spent electrodes. Spent electrolyte would contain metal cations that would have to be removed prior to discharge. The metal cations could be removed by chemical precipitation; however, this would likely generate a HW sludge. Spent electrodes could be sent to a metal refiner for metal recovery or disposed of as a HW.

#### 4.3.4.5 Potential Disqualifiers

Potential disqualifiers of the electrodeposition process include the following:

- Incomplete metals recovery requiring additional wastewater treatment that might generate a hazardous sludge.
- Selectivity/competition.
- Capital and energy costs may be high.

#### 4.3.5 Andco Electrochemical Heavy Metal Removal Process

##### 4.3.5.1 Theory

The Andco electrochemical heavy metal removal process combines electrochemical and chemical precipitation technologies to remove heavy metals from solution. The process, depicted in Figure 4-9, involves passing a direct current through an electrochemical cell containing carbon steel electrodes to produce ferrous ion at the anode and hydroxide ion at the cathode. The ferrous and hydroxide ions diffuse into solution and react forming ferrous hydroxide. Heavy metals are coprecipitated with the ferric hydroxide. The developer states that a smaller volume of sludge is generally produced by the electrochemical process relative to other chemical precipitation processes [49].

##### 4.3.5.2 Developmental Status

The Andco electrochemical heavy metal removal process is a fully developed wastewater treatment technology. Applications include wastewater treatment from a variety of industrial processes including metal finishing, electroplating operations, and printed circuit board manufacturing. Its application to ash treatment would require optimization of the process parameters to the ash extraction solution.

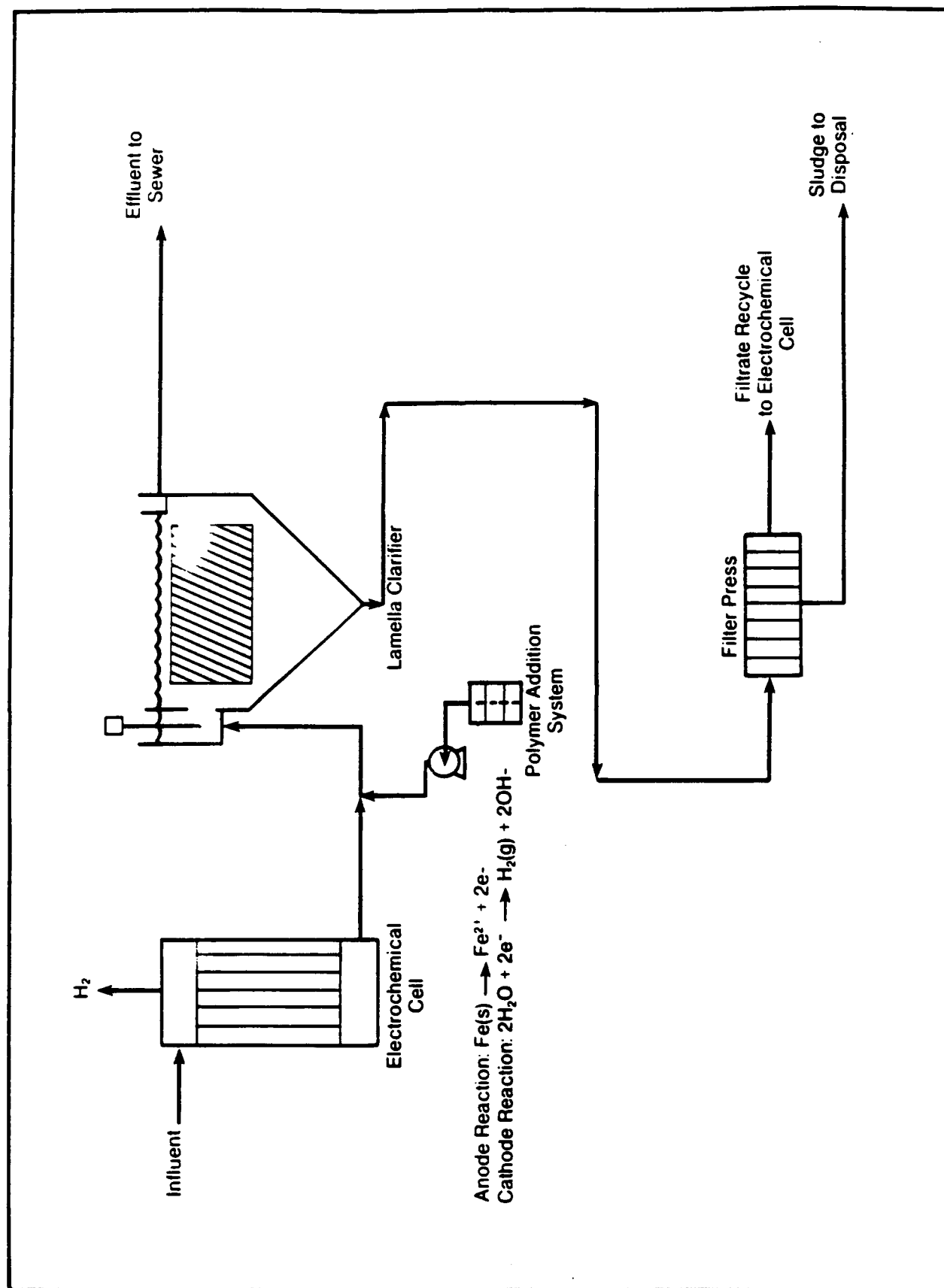


FIGURE 4-9 ANDCO ELECTROCHEMICAL HEAVY METAL REMOVAL PROCESS

#### 4.3.5.3 Effectiveness

The extraction step should be effective in removing heavy metals from the incinerator ash. However, once removed from the ash these metals must be removed from the extract solution. The Andco process is effective in removing heavy metals from aqueous solutions; however, the sludge produced by the process may be a HW.

#### 4.3.5.4 Residuals Treatment/Disposal

Two residual streams are produced by this process: a wastewater stream that may be discharged after pH adjustment (if necessary) and a sludge that may be hazardous due to its metal content.

#### 4.3.5.5 Potential Disqualifiers

Potential disqualifiers of the Andco electrochemical heavy metal removal process include the following:

- The sludge produced by this process may be a HW due to metals content.

### 4.4 THERMAL ASH TREATMENT TECHNOLOGIES

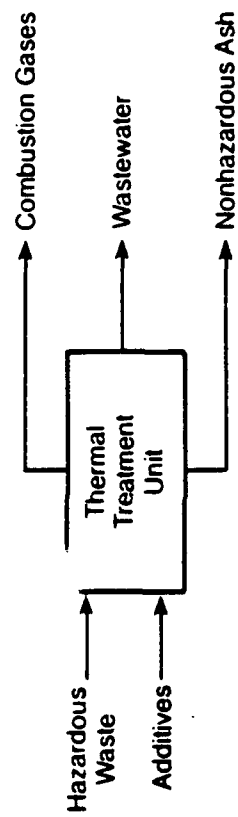
Thermal technologies render the ash nonhazardous by either immobilizing the hazardous constituents in a low leaching matrix or by chemically binding with the metals in the ash. A distinction between thermal ash treatment technologies and extraction and stabilization/fixation technologies is that some thermal ash treatment technologies may be performed during incineration so that a post-incineration ash treatment step is not required.

Figure 4-10a presents a block diagram for thermal ash treatment processes in which the ash treatment steps are carried out during incineration of the waste. Such processes are termed cotreatment processes because they cotreat the ash during the thermal destruction process. Cotreatment processes include the following:

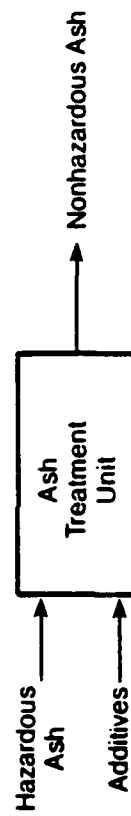
- Roasting/use of incineration additives.
- Slagging kilns.
- Molten glass.

The molten glass process may also be used to treat ash after incineration as shown in Figure 4-10b. These processes are described in the following subsections.





(a) Cotreatment Process



(b) Post Treatment Process

FIGURE 4-10 THERMAL ASH TREATMENT SYSTEM

#### 4.4.1 Roasting

##### 4.4.1.1 Theory

The basic principle of this process is immobilization of the heavy metals in vitrified form. This process immobilizes the heavy metals in the waste by decomposing their hydroxides and salts to form the corresponding oxides and sintering or fusing together the solid particles at temperatures of about two thirds of the melting temperatures. Volatilization of metals at these elevated temperatures is prevented and the formation of a stable product promoted by adding silicates in the form of clay minerals such as kaolinite. Sodium hydroxide and ferric oxide may be added if not present in the waste to yield a viscous melt and raise the boiling point of the metal compounds in the melt [50].

In this process, shown in Figure 4-11, wastes would be fed to a rotary kiln with kaolinite, sodium hydroxide, and ferric oxide. Metals should be immobilized in vitrified form in the bottom ash from the kiln. Combustion gases and entrained fly ash would be treated as in conventional rotary kilns and would generate fly ash and wastewater residuals. Although the additives should reduce metals volatilization, metals with low melting temperatures such as arsenic and mercury may be present in the fly ash.

##### 4.4.1.2 Developmental Status

Bench-scale tests of this process have been conducted on simulated metal hydroxide (electroplating) sludge. Most of the work in this area has been performed in Japan. As a result, there is limited information that is readily accessible on process performance. There is no information on full-scale operations of this process.

##### 4.4.1.3 Effectiveness

Experimental data presented for simulated metal hydroxide sludge seem to indicate that the metals are immobilized in a vitrified form and the residue has very low leachability.

Table 4-5 presents leaching data for three simulated plating sludges roasted at different temperatures and additive ratios. The data indicate the following:

- Roasting is effective in reducing the leachate concentration of high concentration (15 to 100 percent) chromium hydroxide sludges.
- Leaching is generally decreased by increasing the additive ratio and roasting temperature.

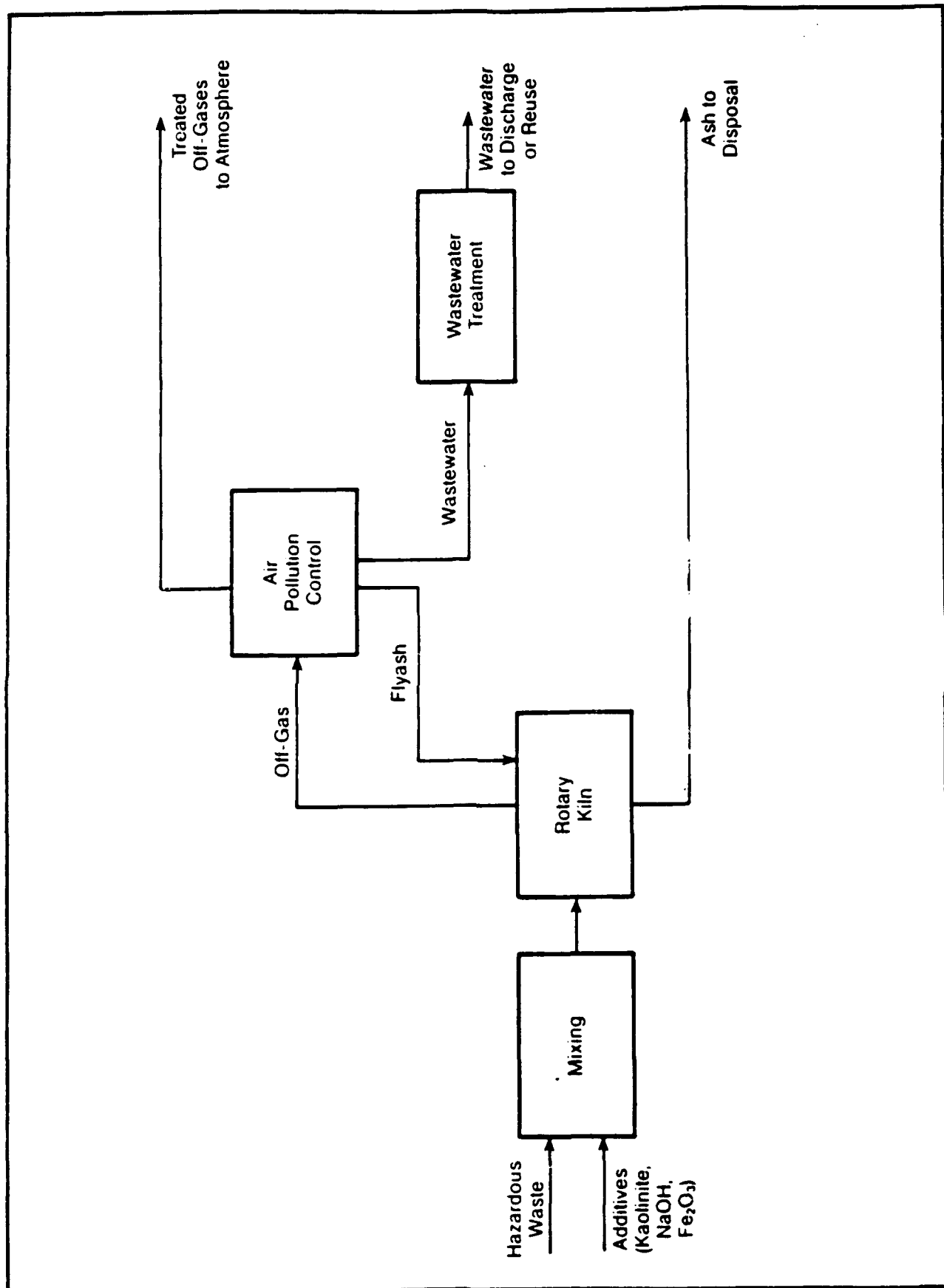


FIGURE 4-11 ROASTING PROCESS

Table 4-5

Slag Leachate Concentrations for Simulated Plating Sludges  
Roasted at Different Temperatures and Additive Ratios

Waste:Clay <sup>c</sup> Ratio	Leachate Concentration <sup>a</sup> (mg/L)							
	Waste A <sup>b</sup>				Waste B <sup>b</sup>		Waste C	
	Cr		Zn		Cr		Cr	
	1830°F	2010°F	1830°F	2010°F	1650°F	1830°F	2190°F	2370°F
3:1	1.7	0.4	0.2	Trace	0.6	0.4	2.0	0.3
3:2	1.2	0.4	0.1	Trace	0.5	0.4	1.2	0.2

Source: [50].

Notes:

<sup>a</sup>Slag samples leached with diluted sulfuric acid (pH=5).

<sup>b</sup>Simulated waste compositions, such as formed in zinc and chromium:

Waste A: Mixed hydroxide sludge of Cr (15%), Zn (65%), and Fe (20%).

Waste B: Mixed hydroxide sludge of Cr (40%), Cu (30%), and Ni (30%).

Waste C: 100% Cr-hydroxide sludge.

<sup>c</sup>Major constituents of clay were SiO<sub>2</sub> (62%), Al<sub>2</sub>O<sub>3</sub> (24%), and Fe<sub>2</sub>O<sub>3</sub> (4%).

#### 4.4.1.4 Residuals Treatment/Disposal

Residuals from this process include all of the residuals associated with rotary kiln incineration including:

- Combustion gases.
- Fly ash.
- Bottom ash.
- Wastewater.

As in rotary kiln incineration, combustion gases and wastewater would be discharged to the atmosphere after treatment. Fly ash generated from particulate control equipment may contain heavy metals, although the roasting additives should reduce metals volatilization. Fly ash might be incorporated into the bottom ash by combining it with the additives and feeding it to the kiln for a second pass. However, if the rate of metals volatilization is too high, the fly ash may require disposal in a HW landfill or additional treatment. If treatment can reduce the metals leachability below EP Toxicity levels or BDAT standards, the vitrified residue may be disposed of in a nonhazardous landfill.

#### 4.4.1.5 Potential Disqualifiers

Potential disqualifiers include the lack of data on specific Navy waste forms and full-scale operational information.

#### 4.4.2 Slagging Kilns

##### 4.4.2.1 Theory

This process is similar to the roasting process in that the basic principle of this process is to remove the bottom ash from a rotary kiln incinerator in vitrified form. This process uses kiln temperatures in excess of 2,000°F in combination with fluxing agents such as glass, lime, and silicates to remove the bottom ash as a glass slag.

In this process, wastes would be fed to a rotary kiln with glass or other fluxing agents. The fluxing agents would melt at kiln temperatures, and bottom ash would be incorporated in the molten slag. The viscosity of the slag is an important design and operating parameter and is dependent on the metals composition of the waste as well as the fluxing agents used. The slag would leave the incinerator in liquid form and be subject to rapid cooling in a water quench. This would form small (less than one inch) glass particles. The slag may be delisted and disposed of in a nonhazardous waste landfill if metals leachability meets delisting criteria. Combustion gases and entrained fly ash would be treated as in conventional rotary kilns and would generate fly ash and wastewater residuals.

#### 4.4.2.2 Developmental Status

Several European rotary kiln manufacturers design their kilns for slagging operation. Although several full-scale units have been constructed in the United States for HW treatment, these units have been designed for specific wastes, and the developer states that the design of these units is still an art because the viscosity of the slag is highly dependent on the chemical composition of the waste.

#### 4.4.2.3 Effectiveness

Discussions with a supplier of this technology indicate that the technology may not produce a nonhazardous slag. Samples of some slags have failed the EP Toxicity test. Test results could not be provided due to client confidentiality. This supplier also stated that most slags would fail the EP Toxicity test [51].

#### 4.4.2.4 Residuals Treatment/Disposal

Residuals from this process include:

- Combustion gases.
- Fly ash.
- Slag.
- Wastewater.

As in rotary kiln incineration, combustion gases and wastewater would be discharged after treatment. Fly ash generated from particulate control equipment may contain heavy metals. Fly ash might be incorporated into the glass slag by feeding it to the kiln for a second pass. However, if the rate of metals volatilization is too high, the fly ash may require disposal in a HW landfill or additional treatment. The slag will contain heavy metals in vitrified form. The slag may be delisted and disposed of in a nonhazardous waste landfill if metals leachability meets delisting criteria.

#### 4.4.2.5 Potential Disqualifiers

Potential disqualifiers include:

- Failure to produce a slag that meets EP Toxicity levels for disposal as a nonhazardous waste.
- Sudden temperature drops in the incinerator or slag discharge mechanism can solidify the slag, preventing ash removal and often resulting in shutdown for major maintenance.

#### 4.4.3 Molten Glass

##### 4.4.3.1 Theory

Use of this process for thermal treatment of HWS was described in Subsection 3.4.2 of this report. This technology achieves metals immobilization by their vitrification in a glass matrix. In this process the ash (or waste) would be fed to a glass furnace. Organics present in the waste would be destroyed in the furnace and afterburner, and inorganics would be retained in the melt that could be removed continuously or intermittently. The melt would be quenched in water to form small (less than one inch) glass particles. Metals should be immobilized in vitrified form in the slag. Makeup glass would be fed to the furnace as necessary.

##### 4.4.3.2 Developmental Status

This technology is in the pilot stage of development. Penburthy International, Inc. maintains a pilot unit in Seattle, Washington. Penburthy has performed tests with municipal solid waste incinerator ashes. Batelle has also performed development work in this field.

##### 4.4.3.3 Effectiveness

Metals should be immobilized in vitrified form in the glass slag; however, results of leaching tests for heavy metals contaminated wastes have not been presented.

##### 4.4.3.4 Residuals Treatment/Disposal

Residuals from this process include:

- Combustion gases.
- Fly ash.
- Slag.
- Wastewater.

As in rotary kiln incineration, combustion gases and wastewater would be discharged after treatment. Fly ash generated from particulate control equipment may contain heavy metals. Fly ash might be incorporated into the glass slag by feeding it to the kiln for a second pass to incorporate it in the glass melt. The slag will contain heavy metals in vitrified form. The slag may be delisted and disposed of in a nonhazardous waste landfill if metals leachability is below the delisting criteria.

#### 4.4.3.5 Potential Disqualifiers

Potential disqualifiers include:

- Lack of performance data on leaching from heavy metal wastes.
- Sudden temperature drops in the slag discharge mechanism can solidify the slag, preventing ash removal and requiring shutdown for major maintenance.

#### 4.5 TECHNOLOGY EVALUATION

The ash treatment technologies identified and described in the previous subsection of this report were evaluated to select the best candidate technologies for research and development. The evaluation used a few key criteria that gauge the technical feasibility of each technology. This section describes the feasibility screening criteria, the evaluation procedures, and the results of the evaluation.

The feasibility screening used the following criteria to evaluate the technologies:

- Treatment effectiveness - Ability to remove or immobilize metals in the ash. At a minimum, the technology must treat the ash to render it nonhazardous by the TCLP or EP Toxicity test. Since more stringent standards may be imposed to delist the ash, technologies that exceed the EP Toxicity target and achieve almost complete metal removal or immobilization are preferred.
- Residual treatment/disposal requirements - If potentially hazardous residuals may be formed, additional treatment processes or secure disposal will be required. This additional treatment/disposal requirement would increase the complexity and/or overall cost of the technology and future risk and liability. A technology that has minimal or no residual waste treatment/disposal requirements would be preferable from environmental, operations, and cost standpoints.
- Process requirements - Technologies that use the existing thermal treatment process are preferable because they would have lower operating and capital requirements than separate ash treatment processes. The need for additional equipment, energy, and chemical requirements increase the complexity of operations and cost of a technology.



- Developmental status - From an implementation standpoint, it would be preferable to use a technology that requires lower R&D effort. Technologies that require minimal R&D time or have already been developed in similar applications would have lower R&D costs.
- Availability of test facilities - The availability of test facilities affects the development of an emerging technology and is necessary for proof-of-concept testing and definition of important variables.

These criteria were selected as the most important criteria that address technical feasibility. The criteria were weighted based on relative importance on a scale of 1 (least important) to 3 (most important) as shown in Table 4-6. Each technology was assigned a performance value on a scale of 1 (poorest performance) to 3 (best performance) for each evaluation criteria. The performance value was multiplied by the criteria's relative importance weighting factor resulting in a score for each criteria. The criteria scores for each technology were summed, and the best choice technologies were identified by the highest total score.

Table 4-7 presents a summary of the results of the ranking evaluation. The table presents the scores for each evaluation criterion for each ash treatment technology. This table indicates the three best choice technologies for ash treatment, in order of preference, are:

1. Cement/lime pozzolan stabilization.
2. Roasting with additives.
3. Microencapsulation and molten glass inclusion.

Microencapsulation and molten glass were ranked equally.

#### 4.6 CONCLUSIONS AND RECOMMENDATIONS

##### 4.6.1 Conclusions

Ten technologies with proven or potential application to ash treatment were identified from a literature search of computerized scientific and engineering databases and a review of standard hydrometallurgical techniques and HW treatment technologies for inorganic wastes. The best choice technologies for future implementation were identified by an engineering evaluation of their effectiveness, process requirements, and R&D requirements. Based on this evaluation, the best choice technologies, in order of preference, are:

1. Cement/lime pozzolan stabilization.
2. Roasting with additives.
3. Microencapsulation and molten glass inclusion.

Microencapsulation and molten glass were ranked equally.

Table 4-6

Ash Treatment Technology Evaluation  
Ranking Criteria and Relative Importance Factors

Criterion Number	Criterion	Relative Importance Factor
1	Treatment Effectiveness	3
2	Residual Treatment/Disposal	3
3	Process Requirements	2
4	Developmental Status	2
5	Availability of Test Facilities	1

Table 4-7

## Summary of Ash Treatment Technology Ranking

Criterion	Relative Importance Factor	Cement/Poz- zolan Sta- bilization		Roasting		Molten Glass		Microencap- sulation		Slagging Kiln		Ferrite Process		Electro- deposition		Ash Amendment		Chemical Precip- itation		Ion Exchange	
		Value Score	Value Score	Value Score	Value Score	Value Score	Value Score	Value Score	Value Score	Value Score	Value Score	Value Score	Value Score	Value Score	Value Score	Value Score	Value Score	Value Score	Value Score	Value Score	Value Score
1. Treatment Effectiveness	3	3	9	3	9	3	9	3	9	2	6	2	6	2	6	2	6	2	6	2	6
2. Residual Treatment/Dis- posal	3	3	9	3	9	2	6	2	6	2	6	2	6	2	6	1	3	1	3	1	3
3. Process Requirements	2	2	4	3	6	2	4	1	2	3	6	1	2	1	2	2	4	1	2	1	2
4. Develop- mental Status	2	3	6	1	2	2	4	3	6	2	4	1	2	1	2	1	2	1	2	1	2
5. Availability of Test Facil- ities	1	3	3	2	2	3	3	3	3	2	2	2	2	2	2	3	3	3	3	3	3
TOTAL		31	28	26	26	24	18	18	18	16	16	9	9	9	9	9	9	9	9	9	9
RANK		1	2	3	3	5	6	6	6	9	9	9	9	9	9	9	9	9	9	9	9

#### 4.6.2 Recommendations

Cement/lime pozzolan stabilization has become extensively commercialized in recent years, and its application can be evaluated on the basis of bench testing for each application. Although it is considered a proven technology with a substantial performance track record, it results in an increase in ash volume and weight, and the long-term performance of stabilized wastes, particularly with respect to long-term acid degradation, is a concern.

Performance data on roasting and molten glass are limited because they are emerging technologies. However, their approach to metals immobilization may offer a less leachable product and better long-term performance than cement/lime pozzolans due to the expected resistance of their products to acidic degradation. Both molten glass and roasting may be expected to produce a denser incineration residual than ash from conventional rotary kiln incineration and may result in overall volume reduction (particularly for molten glass).

While molten glass and microencapsulation were ranked equally, molten glass should offer better long-term stability than microencapsulation. In addition, molten glass can directly treat the waste, which results in lower cost and operational complexity, whereas microencapsulation could only treat the waste after incineration (i.e., ash treatment). These considerations make the molten glass technology preferable to microencapsulation.

Stabilization was rated above roasting and molten glass primarily due to nonperformance factors such as level of development and R&D efforts required to implement the technology. Roasting and molten glass are expected to provide better long-term performance than stabilization.

Therefore, it is recommended that the Navy's R&D efforts in the present context focus on roasting and molten glass, the technologies that show promise of better performance. These technologies would require further development effort prior to implementation.

## SECTION 5

### CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 CONCLUSIONS

5.1.1 The 17 largest Naval waste generating processes were reviewed to identify potentially incineratable waste streams. This review was based on data for calendar year 1985 presented in the Navy's "Hazardous Waste Minimization Initiation Decision Report" [1]. This review concluded that:

- Nine waste streams are potential candidates as future HWs suitable for thermal treatment.
- Many of the other waste generating processes not considered incineration candidates produce wastewaters that are discharged after onsite treatment in the industrial wastewater treatment plant (IWTP).
- The remaining waste streams excluded from consideration as incineration candidates can either be reclaimed, recycled, or otherwise redistributed or can be discharged after wastewater treatment.

5.1.2 An evaluation of the available physical and chemical properties of the nine potentially incineratable wastes identified seven waste streams that were clearly incineratable and two waste streams for which thermal treatment might be required or beneficial. The seven waste streams that are clearly incineratable accounted for about 8,639 tons of the Navy's HWs in 1985 and include the following:

- Spent carbon from ordnance operations.
- Oily sludges from bilge cleaning and emptying.
- Waste solvents and paint residues from painting operations.
- Waste explosives/propellents from munitions demilitarization.
- Oils and sludges from fluids changeout.
- Cleaning solvents.
- Chemical paint stripping solvents and residues.

5.1.3 The two waste streams for which thermal treatment might be required or beneficial to destroy toxic organics accounted for 13,804 tons of the Navy's HW in 1985 and include:

- IWTP sludge.
- Abrasive blasting residues.

5.1.4 Additional data are needed to determine the suitability of incineration for these wastes and the annual quantity of incineratable wastes.

5.1.5 Samples of five of the potentially incineratable wastes streams identified above were obtained for laboratory testing. Tests were conducted to identify the hazardous constituents in the wastes and in the ash from incineration of these wastes. The tests indicated that ash produced from several of these wastes must be disposed of as HWs because they contain concentrations of metals greater than the EP Toxicity test limits. Regulatory standards pertinent to some of these wastes (i.e., IWTP sludge) would require the ash to be treated such that the concentrations of metals leaching from the ash would be less than the EP Toxicity levels, even to allow its disposal in a HW landfill.

5.1.6 The tests described in 5.1.5 also indicated that the IWTP sludge, which is presently disposed of as a HW, may not be hazardous. This particular activity waste could be disposed of as a nonhazardous waste provided additional testing indicates nickel concentrations below regulatory levels of concern.

5.1.7 Since the samples obtained for laboratory testing and analysis were collected from only two facilities, the test results are probably not indicative of these wastes at other facilities. Additional data from several facilities need to be collected to determine representative compositions and quantities of these wastes.

5.1.8 A literature search, conducted to identify technologies capable of removing or immobilizing the hazardous constituents of the ash so that the latter may be delisted and disposed of as nonhazardous waste, yielded ten treatment technologies with potential application. These technologies, subjected to a technical evaluation of their effectiveness, long term performance, and process requirements, are, in order of preference:

1. Cement/lime pozzolan stabilization.
2. Roasting.
3. Molten glass.

5.1.9 Two of the three technologies above, roasting and molten glass, can be used to treat the waste directly as well as to treat the ash from a conventional thermal treatment unit. The third, cement/lime pozzolan stabilization, is solely applicable to ash treatment. The use of roasting and molten glass as a direct waste treatment (or cotreatment) process would result in lower capital equipment cost but possibly higher operating cost as compared to their application in a post-incineration ash treatment process. While stabilization is the only commercial technology of the three recommended, roasting and molten glass should be studied further because of their potential for producing a more inert residue with greater long-term stability in a wide variety of potential environmental conditions.

## 5.2 RECOMMENDATIONS

It is recommended that the Navy continue to pursue its RDT&E program for ash treatment processes.

In order to address the unknowns associated with the treatment/disposal of ash from incineration of the Navy's HWs, it is recommended that a three-phase, integrated R&D program be pursued. Each of the phases is composed of one or more tasks. The objectives and tasks associated with each phase of the R&D program are described in detail in Appendix A, and summarized below.

### Phase 1--Waste Characterization/Source Study

The objective of Phase 1 is to obtain current data on the volumes and physical and chemical characteristics of HWs that can be incinerated for each Navy installation. The study would include a detailed survey of each installation; selection of model waste streams for characterization testing (and subsequent R&D testing); and a report summarizing:

- Waste characteristics and current quantities by waste and installation.
- Projection of HW production rates and characteristics after RCRA conformity has been achieved.
- Selection of future wastes suitable for incineration.
- Preliminary "design basis" waste mix and volume.
- Model future waste streams selected for further study.

This will provide reasonably reliable data projections to serve as the basis for Phase 2 and 3 R&D testing, incineration cost analysis, and future incinerator siting assessment.

## Phase 2--Ash Treatment Technologies Testing and Evaluation

The first task in this phase of the program would be to perform bench-scale tests of the cement/lime pozzolan stabilization process and determine its ability to render the ash generated in Phase 1 nonhazardous. These tests will yield data to establish costs for a "base case" scenario of ash treatment by cement/lime pozzolanic processes.

The second and third tasks of Phase 2 are bench-scale tests that should be performed on the roasting and molten glass processes. These tests should be performed on the raw waste as well as the ash generated from Phase 1. The objectives of these tests would be as follows:

- Determine the performance and viability of these processes.
- Establish whether these processes should be used as ash treatment technologies or as waste treatment technologies.
- Develop data on operating conditions needed for cost estimates for full-scale operations.

Tests would simulate the following:

- Roasting on raw waste streams--Feed would include raw solid/sludge wastes and rotary kiln fly ash in preliminary design basis proportions as well as additives.
- Roasting on incinerator ash--Feed would include rotary kiln bottom ash and fly ash in preliminary design basis proportions as well as additives.
- Molten glass on raw waste streams--Feed would include raw solid, liquid, and sludge wastes in preliminary design basis proportions as well as glass-forming additives.
- Molten glass on incinerator ash--Feed would include rotary kiln bottom ash and fly ash in preliminary design basis proportions as well as glass-forming additives.

These tests would project optimum performance and operating conditions for parameters including:

- Additive rates.
- Temperature.
- Residence time.
- Mixing conditions.



At the end of the above two tasks of testing, cost estimates and other relevant data on full-scale operations of the following technologies would be available:

- Cement/lime pozzolanic treatment of the ash.
- Treatment of ash by roasting.
- Molten glass treatment of the ash.
- Direct treatment of the waste by roasting.
- Direct treatment of the waste by the molten glass process.

These data and costs would be evaluated to identify the optimum process that could be used to cost-effectively treat the Navy's hazardous ash in an environmentally sound manner. The need for a third phase of the R&D program will depend on which process is selected.

#### Phase 3--Ash Treatment Demonstration

The selection of an established process such as cement/lime pozzolanic treatment of hazardous ash could proceed directly to the demonstration phase. The selection of a process that uses an emerging technology, either molten glass or roasting, must be developed by pilot tests in Phase 3 of the R&D program.

## SECTION 6

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## Appendix A

### RESEARCH, DEVELOPMENT, TESTING, AND EVALUATION PLANS

#### A.1.0 INTRODUCTION

In accordance with the conclusions and recommendations of the study, Research, Development, Testing, and Evaluation (RDT&E) plans have been developed to provide the information necessary to implement an ash treatment program for Navy waste.

#### A.1.1 Program Objectives

The objectives of the RDT&E program are to:

- Develop a preliminary "design basis" for the RDT&E for ash treatment.
- Determine the characteristics of rotary kiln incinerator fly ash and bottom ash.
- Determine the performance, viability, operating conditions, and estimated costs for the following processes.
  - Stabilization of ash.
  - Roasting of ash.
  - Molten glass treatment of ash.
  - Roasting of raw waste.
  - Molten glass treatment of raw waste.
- Select the most cost-effective process for ash treatment.

An integrated four-phase plan has been developed to meet these objectives and to enable the Navy to identify the most cost-effective process for ash treatment.

The four phases of the RTD&E testing program are defined as follows:

- Phase 1: Waste Characterization/Source Study
- Phase 2: Ash Generation
- Phase 3: Ash Treatment Technology Testing and Evaluation
- Phase 4: Ash Treatment Demonstration

Phase 1 will be used to develop a preliminary design basis for the evaluation. Phase 2 will be used to generate the required fly and bottom ash for characterization and for Phase 3 testing of ash treatment technologies. Phase 4 will be used to field test the most promising ash treatment technologies identified in Phase 3.

#### A.1.2 Program Resources

Under this plan the RTD&E program will require a variety of resources to meet the objectives of the four-phase plan. Resources will be acquired from engineering laboratories that efficiently offer appropriate specialized services. Contractors can provide conceptual design engineering, pilot and bench testing program management, bench testing services, and laboratory analysis services. This would include the capability to provide pilot rotary kiln and laboratory scale molten glass testing services. A summary of projected manhours and overall cost for Phases 1 to 3 is provided in Table A-1. These are based on an assumed project start of early 1990.

#### A.1.3 Project Schedule

Phases 1 through 3 of the above outlined RTD&E program can be completed within approximately 24 months. An overall project schedule is provided in Figure A-1.

#### A.2.0 PHASE 1: WASTE CHARACTERIZATION/SOURCE STUDY

##### A.2.1 Need

A hazardous waste minimization initiation decision report (IDR) [1] was developed by the Navy that provided extensive data on HWs. The IDR prescribes a detailed course of action that should be followed in order to achieve HW reductions consistent with RCRA mandates and Navy policy. This body of IDR recommended actions will and is having a pronounced effect on the industrial processes the Navy now practices, such that the HWs produced will significantly change with time in character, as well as quantity. As a result, the quantities and characteristics of Navy HWs that will still persist and be available for treatment in the future must be projected. These data are necessary to evaluate, select, and implement a treatment scheme. The Navy

Table A-1

## Summary of Overall RTD&amp;E Program Resources

Phase	1990		1991		1992		Total	
	Hours	\$	Hours	\$	Hours	\$	Hours	\$
1. Waste Characterization/Source Study	1,710	\$177,000	0	0	0	0	1,710	\$177,000
2. Ash Generation/Analysis	300	\$18,000	1,400	\$150,000	0	0	1,700	\$168,000
3. Ash Treatment Testing/Evaluation		0	1,060	\$80,000	2,600	\$323,000	3,660	\$403,000
Total	2,010	\$195,000	2,460	\$230,000	2,600	\$323,000	7,070	\$748,000



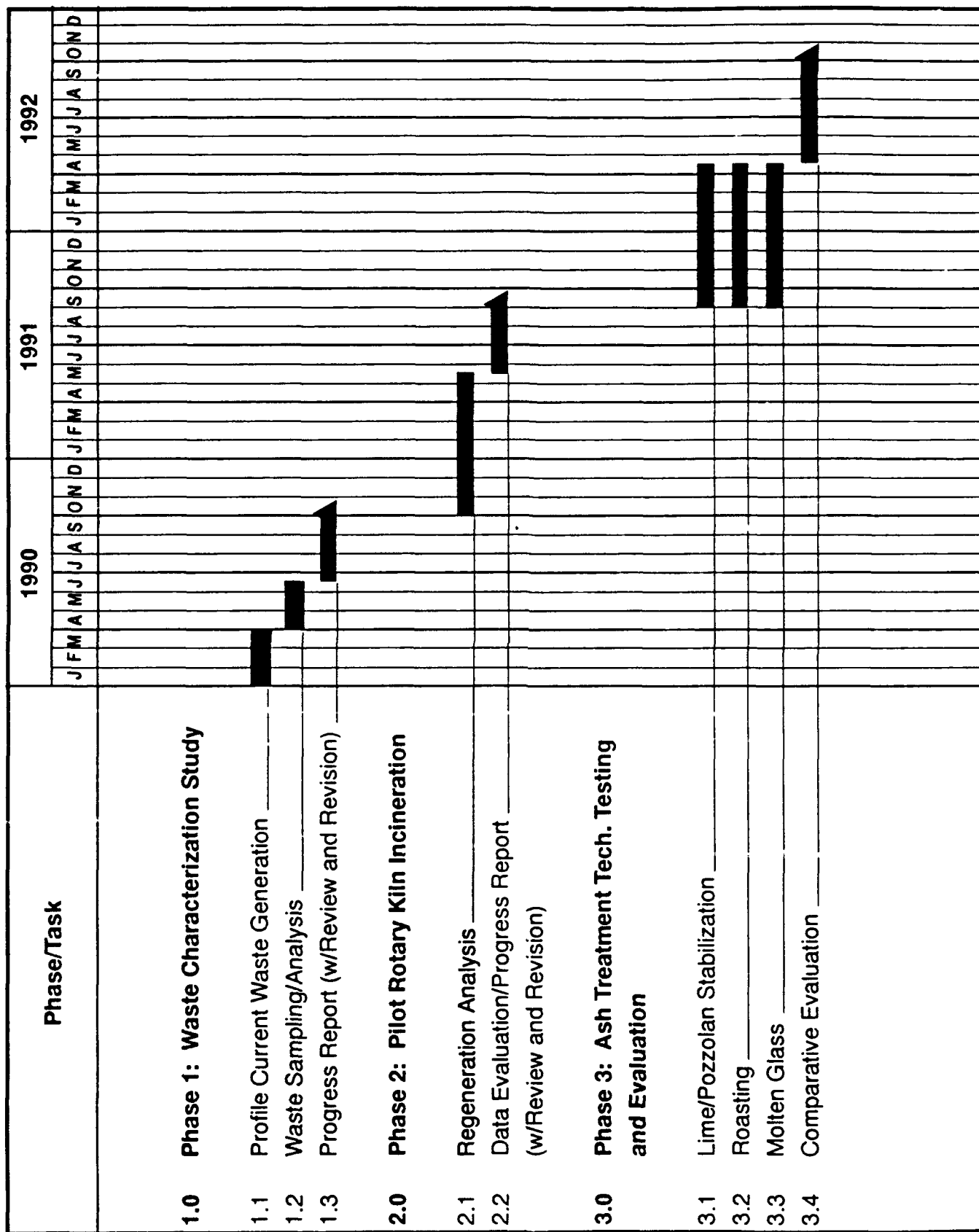


FIGURE A-1. OVERALL PROJECT SCHEDULE

needs to obtain data, specific to thermal treatment requirements, on the quantities and physical and chemical characteristics of HW that would appropriately be incinerated and the facilities that, although optimally modified to be RCRA-conformative, generate these wastes. These data will serve as a basis for Phase 2 and 3 R&D testing.

#### A.2.2 Objective

The objective of Phase 1 is to obtain current data, for wastes produced at each Navy installation, including:

- Waste quantity.
- Physical and chemical characteristics.
- Suitability for incineration.

These data would include all parameters pertinent to thermal treatment and ash treatment. The data will be used to develop a preliminary design basis and to select model waste streams for further testing and evaluation.

#### A.2.3 Technical Approach

Phase 1 will be divided into three tasks, each with defined goals, as follows:

- Task 1: Profile Existing Waste Generation--Relevant existing waste volume and characteristics data will be collected from Navy facilities.
- Task 2: Waste Sampling and Analysis--Waste streams from selected facilities will be sampled and analyzed to provide a database for testing and evaluation of ash treatment technologies.
- Task 3: Interim Progress Report--The report will summarize the results of Tasks 1 and 2 and will identify preliminary design basis and model streams for further study.

The technical approach for these tasks is described below:

##### A.2.3.1 Task 1: Profile Current Waste Generation

Navy facilities will be asked to provide information on waste characteristics and volumes for waste identified as incineratable in this study as well as any other waste that may meet incineration criteria. A survey will be conducted to determine whether additional incineratable waste streams are being generated in significant quantities. Biennial reports and a completed questionnaire on the types of industrial operations present at

each facility, specific HW generation rates and available chemical analyses, and HW manifests will be obtained (for the reporting period) from the environmental specialist at each Navy facility. The name and location of the generating facility and waste types and quantities as identified by EPA Hazardous Waste ID number will be entered into a computer database. The database will be used to aid in identifying additional potentially incineratable wastes based on characteristics or the typical compounds present in wastes with these EPA Hazardous Waste ID numbers and quantities [19] generated by each facility.

#### A.2.3.2 Task 2: Waste Sampling and Analysis

Representative samples of wastes identified as potentially incineratable will be collected. Depending on the physical form of the waste, samples will be analyzed for the selected analytical parameters indicated in Table A-2. This table also identifies the purpose for which these analyses will be used. Due to the differences in the hazardous materials, industrial processes, and practices among facilities, representative samples of each potentially incineratable waste will be collected at facilities based on the waste profile information. These results will be used to confirm the suitability of the wastes for incineration and to select wastes for subsequent phases of the study. In addition, EP Toxicity data to confirm the potential for delisting Industrial Wastewater Treatment Sludge (as discussed in this study) will be collected.

It is currently assumed that the seven waste streams identified as clearly incineratable in this study, and two additional waste streams selected after completing the waste generation profile, will be sampled at four different Navy facilities. The four facilities will be selected based on their representing a particular type of generating process scheme that is distinct from other types. Activity personnel will sample and ship the samples according to protocols provided by NCEL.

#### A.2.3.3 Task 3: Interim Progress Report

The results of Tasks 1 and 2 will be summarized in a Phase 1 progress report. The quantities and chemical and physical characteristics of incineratable waste identified from Tasks 1 and 2 will be used to prepare a preliminary design basis waste composition and volume and identify "model" waste streams that will be used in subsequent testing phases of work.

#### A.2.4 Deliverables

An interim progress report will be prepared that will:

- Summarize waste characteristics and current quantities by waste and installation.

Table A-2

## Waste Characterization Parameters

Analytical Parameter	Waste Forms			Purpose
	Solid	Sludge	Liquid	
Ultimate Analysis %C,H,O,N,S	x	x	x	Calculate theoretical combustion air requirements and product combustion gas flows and approximate composition, material balances.
Heating Value	x	x	x	Energy balance calculations and auxiliary fuel requirements.
Moisture Content	x	x	x	
Metals Scan	x	x	x	Air pollution control requirements, material balances.
Halogen and pH Content	x	x	x	
Ash Content	x	x	x	Furnace design, materials handling, material balances.
Solids Content		x	x	Atomization burner design, materials handling, filterability.
Dissolved		x	x	
Suspended		x	x	
Suspended settling, etc.		x	x	
Particle size		x	x	
Kinematic Viscosity		x	x	
Volatile Organic Compounds (VOC)	x	x	x	Hazardous constituents, PICs.
Base Neutral/Acid Extractable Compounds (BNA)	x	x	x	
Thermal/shock instability <sup>a</sup>	x	x	x	Furnace design.
Optional <sup>b</sup> EP Toxic Metals,	x	x	x	

<sup>a</sup>Explosives wastes only.<sup>b</sup>For selected delisting candidates.

- Confirm wastes suitable for incineration.
- Identify a design basis waste mix and generation rate.
- Identify model waste streams for further study.

#### A.2.5 Resources

The Phase 1 study can be conducted by NCEL using engineering and analytical support services. This phase of study will be conducted with the assistance and cooperation of the responsible environmental coordinators at each Navy installation. The projected costs and manhours for each task of Phase 1 of the RTD&E program are summarized in Table A-3.

#### A.2.6 Schedule

Phase 1 of the RTD&E program will be completed within 9 months. Details of the Phase 1 schedule are provided in Figure A-2.

### A.3.0 PHASE 2: PILOT ROTARY KILN INCINERATION AND ASH GENERATION

#### A.3.1 Need

Sufficient quantities of bottom ash and fly ash need to be generated for subsequent use in Phase 3 of the RDT&E program. All of these needs can be met by the use of a pilot-scale rotary kiln incinerator operated within a predetermined range of conditions. The characteristics of residues with regard to land ban regulations and potential delisting will be determined.

#### A.3.2 Objectives

The objectives of Phase 2 are: (1) to generate bottom ash and fly ash representative of the ash produced during the anticipated normal incineration of the model waste streams, identified in Phase 1; (2) to analyze the ash for landfill-ban and HW listing/delisting characteristics; and, use in Phase 3.

#### A.3.3 Technical Approach

Phase 2 will be divided into three tasks, each with defined goals, as follows:

- Task 1: Pilot-Scale Rotary Kiln Incineration -- Conduct pilot-scale incineration operations on Navy's design-basis waste under defined operating conditions.
- Task 2: (Concurrent with Task 1) Analysis of Incinerator Ash -- Obtain ash characteristics data and sufficient ash to conduct Phase 3 tests.

Table A-3

Resources Projected for Phase 1 of the RTD&E Program:  
Waste Characterization/Source Study

Task	1990	
	Labor Hours	\$
1. Profile Current Waste Generation	900	\$65,000
2. Waste Sampling and Analysis	520	\$92,000
3. Interim Progress Report	290	\$20,000
Total	1,710	\$177,000

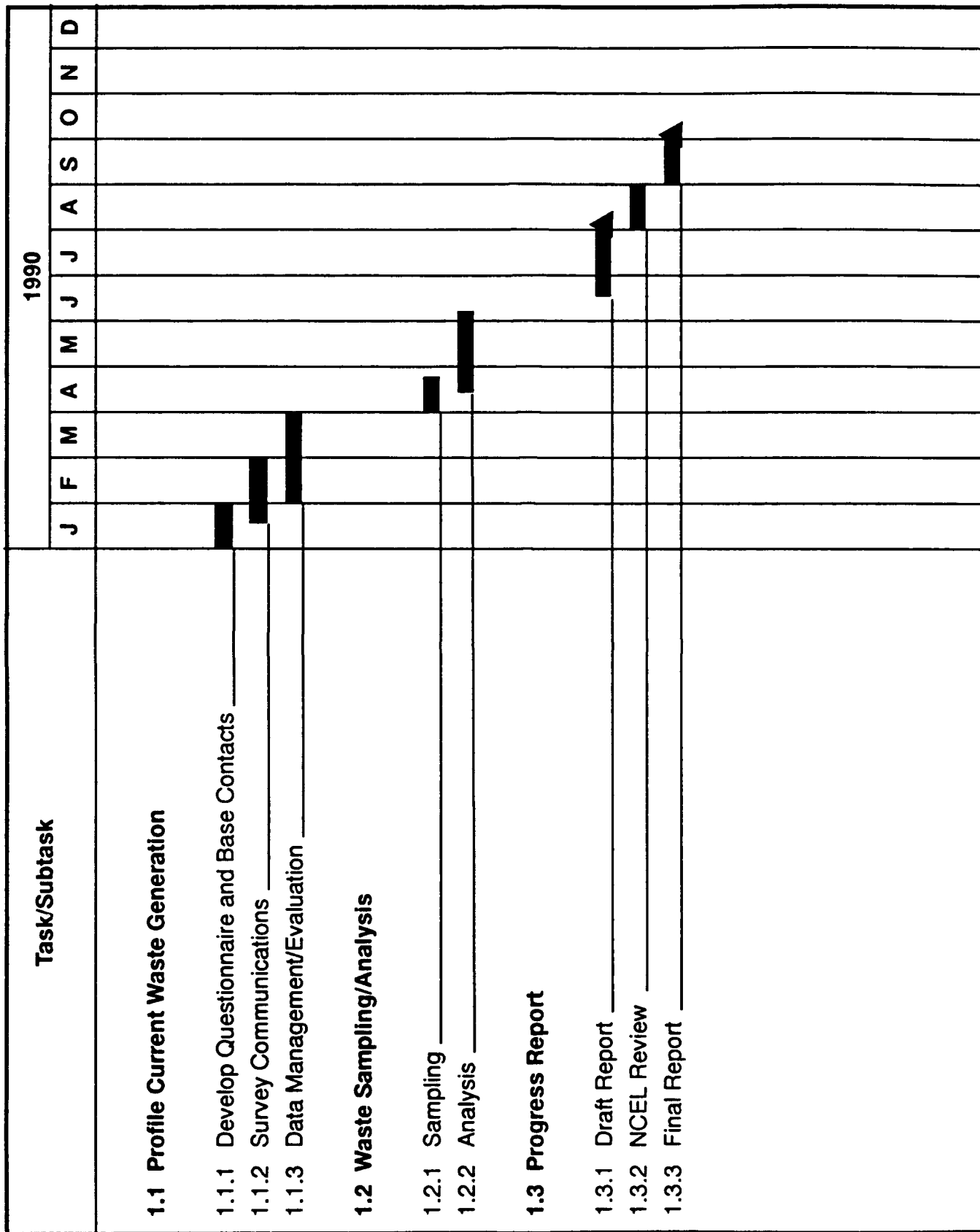


FIGURE A-2. PHASE 1: WASTE CHARACTERIZATION/SOURCE STUDY DETAILED SCHEDULE

Task 3: Interim Progress Report -- Summarize the results of Tasks 1 and 2.

The technical approach for these tasks is described below:

A.3.3.1 Task 1: Pilot-Scale Incineration

The waste, determined from Phase 1, will be incinerated under conditions meeting Federal, State, and Local Government requirements. The bottom ash and fly ash will be collected, sampled, and stored for subsequent treatment in Phase 3.

A.3.3.2 Task 2 (Concurrent with Task 1): Analysis of Incinerator Ash

The analytic measurements and tests listed in Table A-4 will be performed on the bottom ash and fly ash generated in Task 1. The results of these tests will be added to the data base.

A.3.3.3 Task 3: Data Evaluation/Interim Progress Report

The results of Tasks 1 and 2, to be used for Phase 3 testing, will be evaluated.

A.3.4 Deliverable

An interim report will be prepared that will summarize the results of the incinerator tests.

A.3.5 Resources

A contractor will be used to incinerate waste and deliver generated ash to an analytical laboratory for testing. Resources required will include:

- Suitable rotary kiln incinerator permitted to generate ash for R&D.
- Appropriately trained operating and supervisory personnel.
- Laboratory for ash analysis.

The projected costs and manhours for each task of Phase 2 of the RTD&E program are summarized in Table A-5.

A.3.6 Schedule

Phase 2 of the RTD&E program will be completed within 11 months of completion and acceptance by Navy of Phase 1 of the program. Details of the schedule are provided in Figure A-3.



Table A-4

Analytical Tests on Bottom and Fly Ash Generated from  
Incineration Pilot Tests

Analytical Parameter	Purpose
EP Toxicity Metals	Determine constituents of ash that may leach to provide basis for ash treatment requirements.
Total Metals	Fate of metals, material balances.
VOC, BNA	Confirm waste destruction and support possible delisting of ash.
TCLP Leachate VOC, BNA	For land ban wastes, determine whether residues can be landfilled.
Moisture Content, Bulk Density, Angle of Repose	Material handling and storage facility design.

Table A-5

Resources Projected for Phase 2 of the RTD&E Program:  
Pilot Rotary Kiln Incineration and Ash Generation

Phase	1990		1991		Total	
	Hours	\$	Hours	\$	Hours	\$
1. Incineration	300	\$18,000	400	\$52,000	700	\$70,000
2. Analysis of Incinerator Ash	0	0	500	\$70,000	500	\$70,000
3. Data Evaluation/ Interim Progress Rep	0	0	500	\$28,000	500	\$28,000
Total	300	\$18,000	1400	\$150,000	1,700	\$168,000

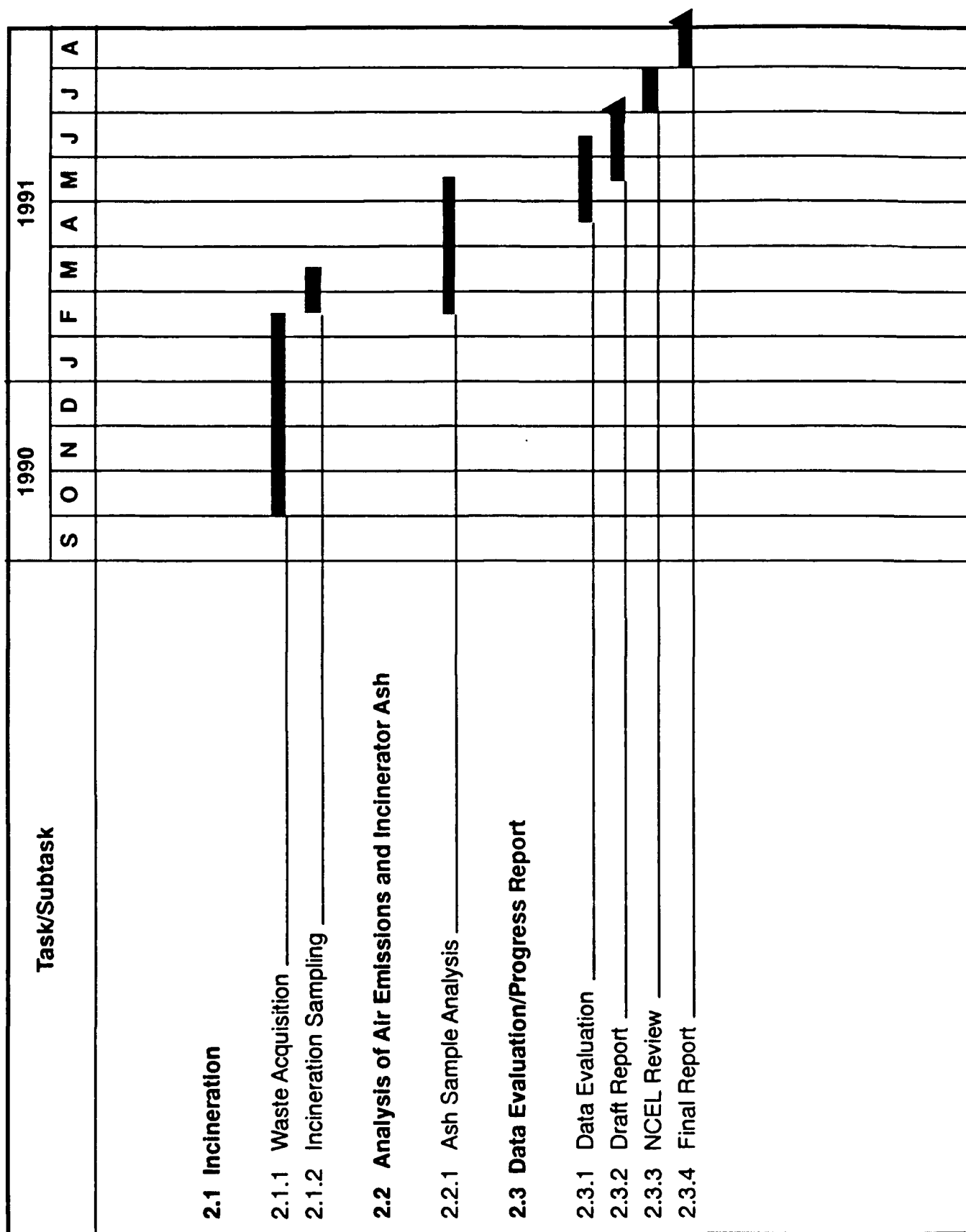


FIGURE A-3. PHASE 2: PILOT ROTARY KILN INCINERATION DETAILED SCHEDULE

#### A.4.0 PHASE 3: ASH TREATMENT TECHNOLOGY TESTING AND EVALUATION

##### A.4.1 Need

Thermal treatment of HWS produces ash that is considered HW under current regulations, unless delisted based on a demonstration of detoxification or reduction of mobility. The ash also may be characteristically hazardous due to EP Toxicity (i.e., leachable metals). In order to reduce the toxicity, mobility, and future liability associated with thermal residue land disposal, it is desirable to treat the ash to produce a nontoxic product that can be safely disposed of. The tests performed in Phase 3 will provide a sound basis for evaluation and design the optimal treatment method(s) for ashes generated by incineration in Phase 2 or the use of cotreatment processes.

##### A.4.2 Objectives

The objectives of tests conducted in Phase 3 are to:

- Determine the viability and performance of three promising waste/ash treatment technologies.
- Generate data to evaluate the application of the technologies for rotary kiln ash treatment or as stand-alone waste treatment technologies.

##### A.4.3 Technical Approach

Phase 3 will be divided into four tasks. The first three tasks are bench-scale laboratory experiments for the three candidate ash/waste treatment technologies:

- Cement/Lime Pozzolan Stabilization.
- Roasting.
- Molten Glass.

These three tasks will be conducted in parallel; Task 4 will consist of an evaluation of the results of testing and an overall process scheme evaluation to identify the best alternative available. The technical approach for these tasks is described below:

###### A.4.3.1 Task 1: Cement/Lime Pozzolan Stabilization Testing

Cement/lime pozzolan stabilization processes will be tested in laboratory experiments to determine the ability of this technology to render the ash generated during Phase 2 activities

nontoxic. A set of bench-scale tests will be performed wherein various weight mixtures of ash-pozzolan will be blended for all applicable combinations of ash and pozzolan. The resulting "stabilized" matrix will be tested for leachability of the relevant TCLP organic compounds and EP Toxicity metals to evaluate the treatment effectiveness. Results will be added to the database used in the overall ash treatment performance assessment. We currently assume that 12 ash/pozzolan batch compositions will be tested.

#### A.4.3.2 Task 2: Roasting Testing

This task will evaluate the roasting technology in two potential process schemes: treatment of the ash (produced in Phase 2) and direct sequential treatment of the wastes collected in Phase 1.

Roasting will be evaluated as follows:

- Ash Treatment: Bench-scale tests will be conducted, using crucibles and a high temperature (1,300°C) oven, wherein various weight mixtures of ash and roasting additive will be blended and fired at various temperatures. The resulting stabilized product will be tested for metals leachability by the EP Toxicity procedure and other selected parameters provided in Table A-2. We currently assume that 20 ash/additive mixtures will be tested.
- Waste Cotreatment: Bench-scale tests will be conducted in the apparatus discussed above. Various weight mixtures of solid/sludge waste, ash, and roasting additive will be blended and fired at various temperatures. The resulting stabilized product will be tested by the EP Toxicity procedure and other selected procedures on Table A-2. We currently assume that 20 waste/additive mixtures will be tested.

Results will be used in the overall ash treatment performance assessment.

#### A.4.3.3 Task 3: Molten Glass Testing

This task will evaluate the molten glass technology in two potential process schemes: treatment of the ash produced in Phase 2 and direct sequential treatment of the wastes collected in Phase 1.

The tests will be conducted in a bench-top electric molten glass pilot unit that uses the same process scheme as a full scale unit. All glass-matrix products will be tested for metals leachability by the EP Toxicity procedure.

Molten glass will be evaluated as follows:

- Ash Treatment: Bench-scale tests will be conducted at various weight loadings of ash and glass-forming additives and various temperatures as recommended by the process developer.
- Waste Cotreatment: Various weight loadings of raw waste and glass-forming additives will be treated in a bench-scale unit at various temperatures, in addition to the optimal temperature. Special attention will be paid to the treatment of liquid wastes (by this unit) for evaluation of its use and any unusual design considerations. The resulting glass matrix products will be analyzed for the parameters listed in Table A-2, and the results will be added to the database so that performance criteria can be determined.

#### A.4.3.4 Task 4: Comparative Evaluation and Selection

The results of the alternative ash treatment/cotreatment process bench-scale studies will be evaluated to determine whether adequate performance can be achieved. Preliminary process cost estimates will be developed for the technologies and process schemes that are found to be effective. Based on the performance and cost projections, the most cost-effective process scheme that can treat the Navy's ash in an environmentally sound manner will be recommended. The need for a fourth phase of the RTD&E program will depend on which process is selected.

#### A.4.4 Deliverable

A final report will be produced summarizing the results of all analytic work in tabular form grouped under headings dictated by the tests that were performed. The report will include:

- Parametric comparisons between various operating conditions for the technologies that were tested.
- Comparison between the technologies for effectiveness in rendering the waste/ash nontoxic.
- Identification of the process schemes that are most effective.
- Development of process flow diagrams and major equipment sizing for the technologies and process schemes that were found to be effective.

- Projected cost estimates (+50 percent, -30 percent) for the technologies and process schemes that were found to be effective.
- Recommended waste/technology schemes based on performance, cost, and logistics of Navy waste production and location.

#### A.4.5 Resources

NCEL will provide overall management and coordination of the bench-scale Phase 3 testing. An NCEL contractor will conduct bench-scale stabilization and roasting tests, as well as specialized equipment and testing services related to molten glass treatment. A contractor will be used to perform laboratory analysis services. The projected costs and manhours for each task of Phase 3 of the RTD&E program are summarized in Table A-6.

#### A.4.6 Schedule

Phase 3 of the RTD&E program will be completed within 13 months of completion and acceptance by Navy of Phase 2 of the program. Details of the schedule are provided in Figure A-4.

#### A.5.0 PHASE 4: ASH TREATMENT DEMONSTRATION

The selection of an established process such as cement/lime pozzolan treatment of ash could proceed directly to the field test. The selection of a process that uses an emerging technology, either molten glass or roasting, must be developed by pilot tests in Phase 4 of the R&D program.

Table A-6

Resources Projected for Phase 3 of the RTD&E Program:  
Ash Treatment Technology Testing and Evaluation

Phase	1991		1992		Total	
	Hours	\$	Hours	\$	Hours	\$
1. Cement/Lime Pozzolan Stabilization	300	\$22,000	300	\$46,000	600	\$68,000
2. Roasting	360	\$29,000	540	\$64,000	900	\$93,000
3. Molten Glass	400	\$29,000	300	\$104,000	700	\$133,000
4. Comparative Evaluation and Selection	0	0	1,460	\$109,000	1,460	\$109,000
Total	1,060	\$80,000	2,600	\$323,000	3,660	\$403,000



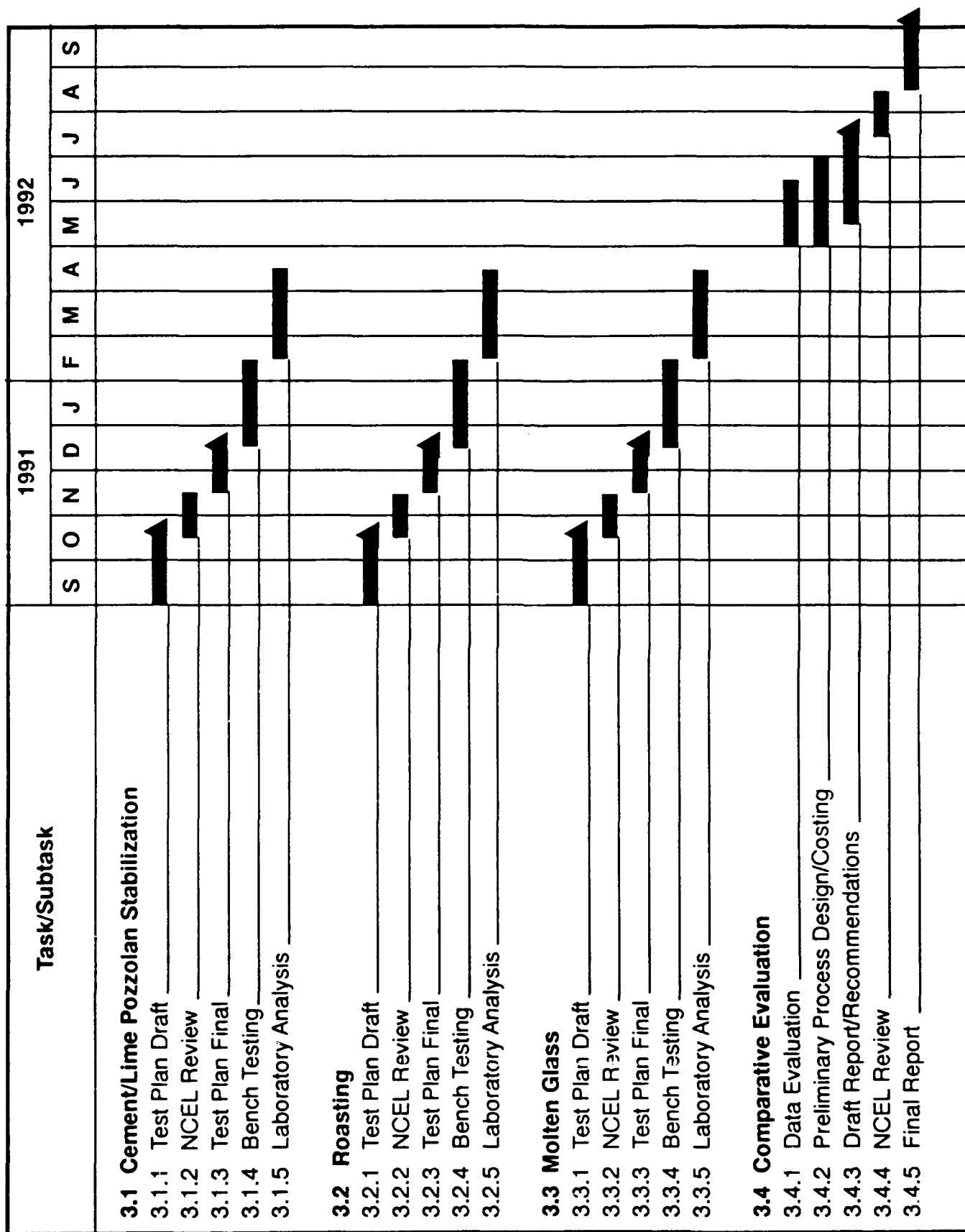


FIGURE A-4. PHASE 3: ASH TREATMENT TECHNOLOGY TESTING

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Port Hueneme, CA 93043-5003**

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